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THE UNIVERSITY OF ALBERTA

I. FREE RADICAL CYANATION
II. POLAR EFFECTS AND THE VISCOSITY DEPENDENCE OF TERMINATION REACTIONS OF SIMPLE ALKYL RADICALS

by

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A THESIS

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TO MY FAMILY

ABSTRACT

PART I

The peroxide-initiated free radical chain cyanation of several hydrocarbons with methyl cyanoformate has been investigated. The reaction is proposed to proceed through the intermediacy of an iminyl radical formed by the addition of an alkyl radical to the carbon-nitrogen triple bond. The resulting iminyl radical undergoes β-scission to form the alkyl cyanide, carbon dioxide, and a methyl radical which subsequently carries the chain. Only traces of products, possibly arising from carbonyl addition, were observed.

The peroxide promoted reaction of the reagent with 2,4-dimethylpentane yielded only minor amounts of the three possible cyanides (20%), but gave as the major product in 55% yield, the difunctionalized heterocycle, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene. A reaction pathway for the formation of the cyclized product was proposed to proceed by addition of the initially formed tertiary alkyl radical to the cyano triple bond to form the iminyl radical, the same radical used to rationalize the chain cyanation; internal hydrogen abstraction by the iminyl radical formed by this addition followed by addition of the new tertiary radical to the nitrogen of the imine double bond and disproportionation of the new radical to yield the difunctionalized cyclic

product in a nonchain process. Consistent with this mechanism was the observation that a modest yield (22%) of difunctionalized cyclic product, 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene, was formed from the reaction of cyanogen with 2,4-dimethylpentane.

The benzoyl peroxide initiated cyanation reaction of several hydrocarbons using oxalyl cyanide and carbonyl cyanide was attempted. The reactions proceeded by a nonchain mechanism, and only with cyclohexane, was a moderate yield (~50%) of cyanation product (cyclohexyl cyanide) obtained. The reactions failed to proceed to any appreciable extent (<1%) with several other substrates, such as 2,3-dimethylbutane and 2,4-dimethylpentane. The formation of a dark brown precipitate, paracyanogen, in reactions of carbonyl and oxalyl cyanide with all of the investigated hydrocarbons, indicated that cyanide radicals are produced in these reactions. It appears that cyanide radicals are not good chain carriers, and further that carbonyl and oxalyl cyanide are not useful as cyanating reagents. A plausible mechanism for the formation of cyclohexyl cyanide has been discussed. The reaction is proposed to proceed by the addition of a cyclohexyl radical to the carbon-nitrogen triple bond of the cyanide group to form an iminyl radical intermediate which undergoes β-scission to form cyclohexyl cyanide.

PART II

The photodecomposition of azoisopropane (AIP, 0.1 M), in solutions of substituted toluenes, which contained thiophenol-d (0.5 M) yielded propane, propane-2-d, propene, phenyl propyl-2-d sulfide, nitrogen and small amount of isopropyl hydrazone. A material balance, based on isopropyl radicals produced, showed that very little, if any, of the propane formed was the product of an abstraction reaction from the solvent toluene. The propane, instead, was formed primarily from a cage disproportionation reaction. The relative rates of formation of propane and propane-2-d, produced by abstraction from thiophenol-d (0.5 M), varied in a uniform manner from substrate to substrate. The values of these relative rate constants correlated with, σ, substituent constants. Since it had been previously demonstrated for the substituted toluenes that the log of their relative viscosities correlated with their, σ, substituent constants, it was clear that the apparent correlation of the relative rates in the present system could be related to the viscosity of the media. The importance of cage disproportionation was further substantiated since, a plot of 1/cage yield correlated with the fluidity ($1/\eta$) of the solvents.

Further, it is demonstrated for both isopropyl

radicals and tert-butyl radicals that the product distributions in solvents (benzenes) and toluenes are the same. In the presence of thiophenol, neither isopropyl radicals nor tert-butyl radicals add to the aromatic ring.

The viscosity dependence of the product distribution obtained from the self reaction of tert-butyl radicals generated as encounter pairs had previously been explained using a collision model.

A study of the azo decomposition reaction afforded an opportunity to compare the viscosity dependent behavior of radical pairs, generated as geminate pairs to that reported for encounter pairs.

In order to investigate the dependence of the cage disproportionation-combination ratio of tert-butyl radicals on the media, the photodecomposition of 2,2'-azoisobutane (0.1 M) was carried out in inert solvents using thiophenol (0.5 M) as a scavenger. The k_d/k_c ratios observed were almost identical to those obtained from the reaction of encounter pairs over a range of viscosities from 0.48-2.67 cP. The similarity of values obtained at these low viscosities suggests that the tert-butyl radical pairs, generated from the azo photolysis, are formed with sufficient rotational energy to appear to be randomly oriented. Over the range of viscosities from 12-808 cP the ratio of termination rate

constants does not increase significantly, and it appears that the free reorientational model fails to predict the values of k_d/k_c. The behavior of the geminate pairs in the very viscous solvents suggests that a random array of collisional orientations is not available to the radical pairs at birth. The orientation of the radicals upon formation appears to favor the combination process.

The plot of cage efficiency (1/cage yield) for tert-butyl radicals vs. fluidity of the solvents, $(1/\eta)$, gave a nearly linear correlation. At high viscosity some deviation from linearity was observed.

Finally, the viscosity dependence of the k_d/k_c ratios for isopropyl radicals is discussed qualitatively using a collision model similar to that used for the tert-butyl radicals.

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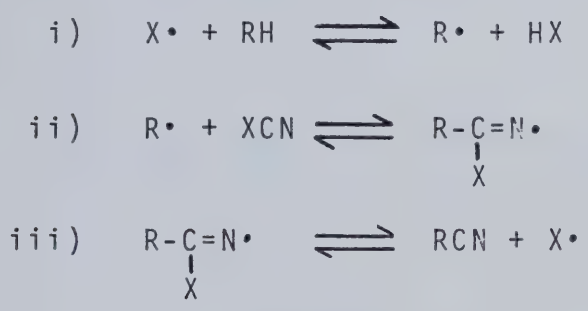
INTRODUCTION

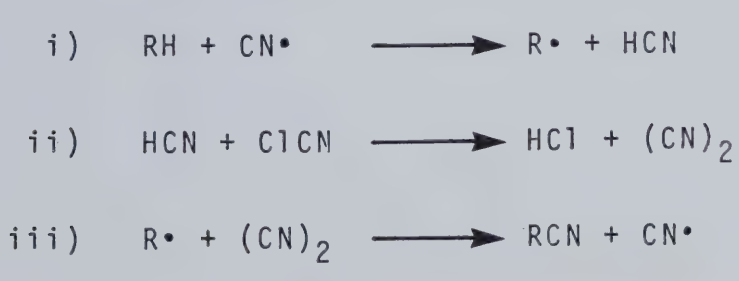
PART I

Free radical cyanation of alkanes using cyanogen chloride, ClCN, was first reported by Müller and Huber[1] and the mechanism of this reaction was extensively studied by Tanner et al.,[2,3,4] who used both cyanogen chloride, ClCN, and cyanogen bromide, BrCN, as cyanating agents. The mechanism of this benzoyl peroxide initiated reaction was shown to involve the reversible sequence depicted in Scheme 1.



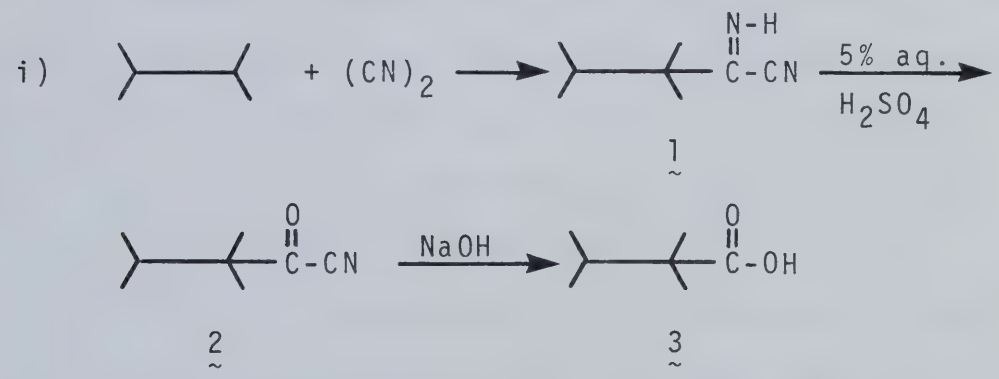
(SCHEME 1)

During the course of the investigation of the mechanism of this reaction, an alternative chain mechanism was considered for the formation of the alkyl cyanide.[2] This involved hydrogen abstraction by a cyanide radical as shown in Scheme 2.



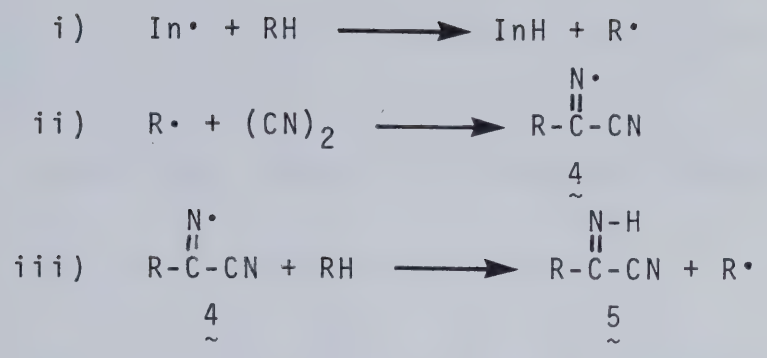
(SCHEME 2)

The proposed radical displacement on cyanogen was investigated by studying the radical chain reaction of cyanogen with 2,3-dimethylbutane in the presence of catalytic amounts of benzoyl peroxide. Instead of the anticipated tertiary cyanide, which was the product from the reaction with the cyanogen halides, a high yield of a 1:1 adduct (1) of the hydrocarbon and cyanogen was obtained. This was the only observed product (Scheme 3).



(SCHEME 3)

The iminocyanide (1) could be quantitatively converted by hydrolysis to the acyl cyanide (2) or to the corresponding carboxylic acid (3). The chain mechanism, depicted in Scheme 4, was proposed for the formation of the adduct.



In = Benzoyl peroxide.

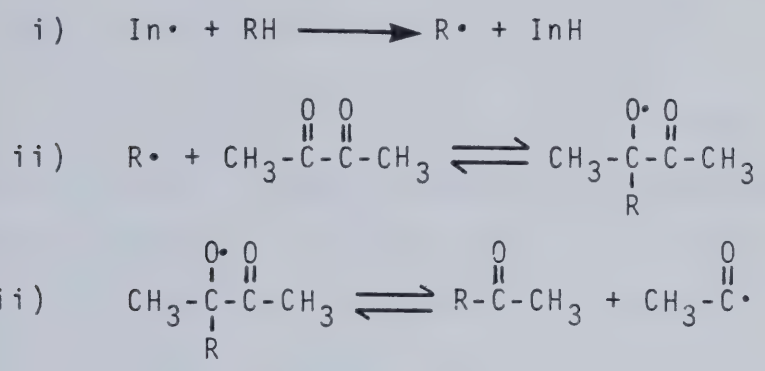
(SCHEME 4)

This mechanism implies that the cyanide group is not a good leaving group since the intermediate iminocyanide radical (4) abstracts a hydrogen atom to give the iminocyanide (5) rather than undergoing β-scission to give the alkyl cyanide and a cyanide radical.

The selective homologation of a hydrocarbon by one or two functionalized carbon atoms has some potential synthetic utility. Although the cyanation reactions with cyanogen halides were successful they were of limited utility because the corresponding alkyl halide, RX, was formed as another major product thereby limiting the yield of RCN. The alkyl halide, RX, was shown to arise through the oxidation, by benzoyl peroxide, of the hydrogen halide formed in step (i), Scheme 1, and the subsequent halogenation of the substrate by molecular chlorine[3] or bromine.[4] Unfortunately the analogous reaction with cyanogen failed when tried with a large number of other substrates.[2]

While these studies were in progress, Bentrude[5]

reported a free radical addition to biacetyl. The reaction sequence which leads ultimately to the formation of acetylation products is shown in Scheme 5.



(SCHEME 5)

However the low to moderate yield of acetyl products, using high concentration of benzoyl peroxide, suggested either a short kinetic chain or the absence of a chain mechanism. These reactions are of interest because of their possible synthetic applications.

Subsequently, Tanner and Das[6] attempted the synthesis of pyruvyl cyanide, $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CN$. It was thought, by analogy to Bentrude's acylation reaction,[5] that this substrate could be used as a possible reagent for the cyanocarbonylation of hydrocarbons:

(1)

It was hoped that this transformation, which leads to the formation of acyl cyanide such as (2), could be effected using different substrates, since the attempted transforma-

tion using cyanogen were only successful with 2,3-dimethylbutane.

$$R\cdot + NCCN \longrightarrow R\text{-}\overset{\overset{NH}{\|}}{C}\text{-}CN \longrightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}CN \qquad (2)$$

R = 2,3-dimethylbutane.

However, when the synthesis of pyruvyl cyanide was attempted from the corresponding acyl chloride and cuprous cyanide, a reaction known to be successful with other acid halides,[7] only acetyl cyanide was obtained. Since the acetyl cyanide could be formed from acetyl chloride under these conditions,[7] the possibility of the fragmentation of pyruvyl chloride to form acetyl chloride was investigated.[6]

In cyclohexane solution, pyruvyl chloride, in the presence of benzoyl peroxide (5%) and light or AIBN (8%), not only gave acetyl chloride, but also products resulting from a series of radical displacement reaction on pyruvyl chloride. These products were cyclohexane carboxylic acid chloride, cyclohexyl methyl ketone, and cyclohexyl chloride along with hydrochloric acid, methane and carbon monoxide. The product distributions obtained in these reactions are listed in Table (1).

TABLE 1

Products from the Initiated Reaction of Pyruvyl Chloride (0.2 M) in Cyclohexane[6]

Initiator	Temp. °C	CH_3COCl	$C_6H_{11}COCH_3$	$C_6H_{11}COCl$	$C_6H_{11}Cl$
Bz_2O_2 (5%)	98	50.3	10.0	39.5	3
light	40	54.3	10.2	35.5	5.0
AIBN (8%)	40	75	3	17	trace

The preference for addition of the alkyl radical to the electron deficient carbonyl is evident from the 1:3.8 ratio of cyclohexyl methyl ketone to cyclohexyl carboxylic acid chloride, the products which were obtained from the β-scission of the corresponding alkoxy radical. Little direct radical displacement on chlorine was observed as is evident by the low yield of cyclohexyl chloride found in the reaction mixtures. Several radical chain sequences were proposed to rationalize the results observed (Scheme 6).

Net Radical Chains:

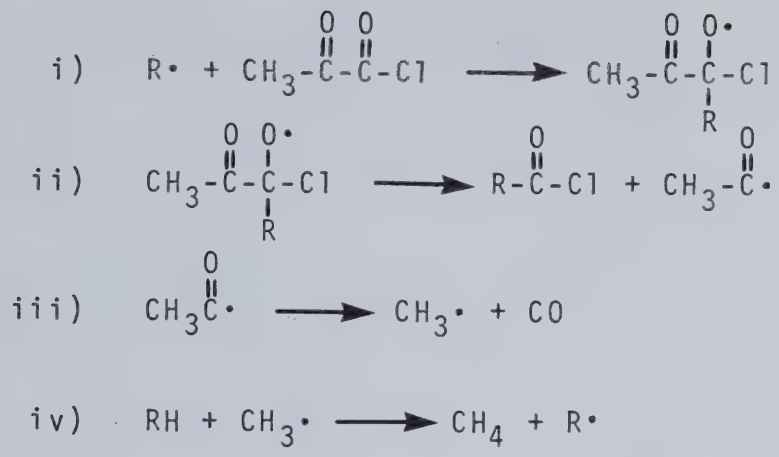
a: $R = C_6H_{11}$

i) $R\bullet + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow CH_3-\overset{O\bullet}{\overset{|}{\underset{R}{C}}}-\overset{O}{\overset{\|}{C}}-Cl$

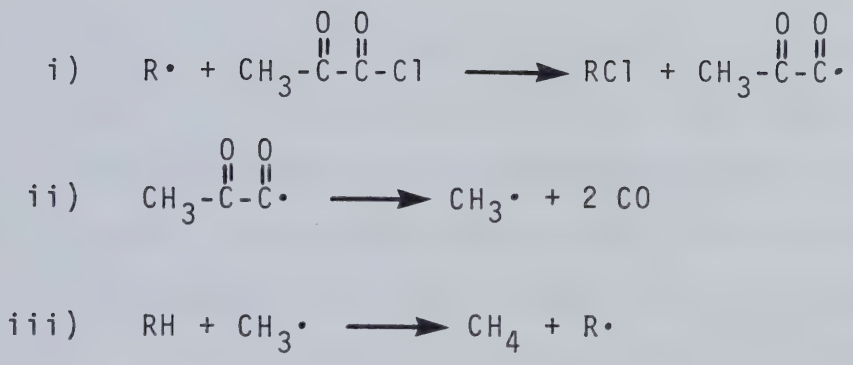
ii) $CH_3-\overset{O\bullet}{\overset{|}{\underset{R}{C}}}-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_3 + CO + Cl\bullet$

iii) $RH + Cl\bullet \longrightarrow R\bullet + HCl$

b:



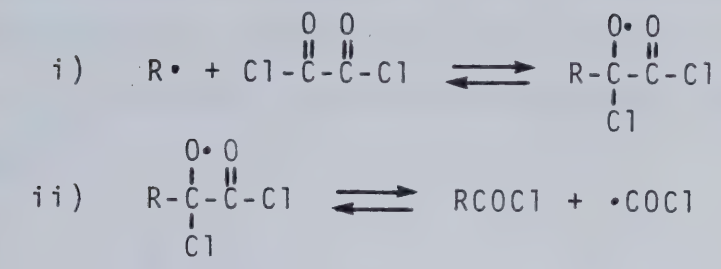
c:



(SCHEME 6)

The direct introduction of functional groups such as the carboxyl group into saturated hydrocarbons was first investigated by Kharasch and Brown.[8] They reported the chloroformylation of a series of hydrocarbons using oxalyl chloride. The reactions were initiated photochemically or by using benzoyl peroxide.

The proposed mechanism is shown in Scheme 7 .

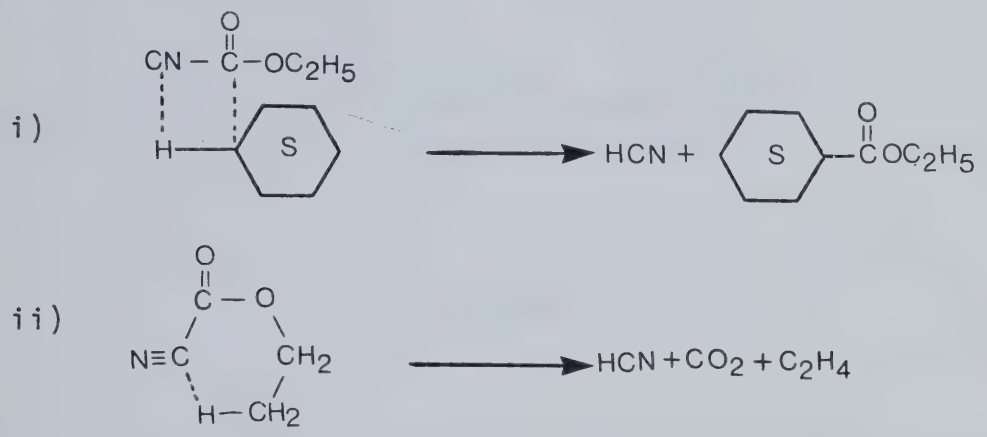


(SCHEME 7)

This method was later used, for example, in the chloroformylation of [2.2] paracyclophane[9] and adamantane.[10] A low yield of chloroformylation product was obtained when aralkyl hydrocarbons were used. This was attributed to an unfavorable equilibrium position, as in Step (i), Scheme 7. The position of the equilibrium naturally depends on the stability of the radical R·.

The photolytic decomposition of ethyl cyanoformate in cyclohexane produced cyclohexyl cyanide (2%), ethyl cyclohexane carboxylate (19%), and ethyl cyclohexaneglyoxylate (3%). The gaseous products consisted of carbon dioxide, hydrogen cyanide and ethylene.[11,12] The formation

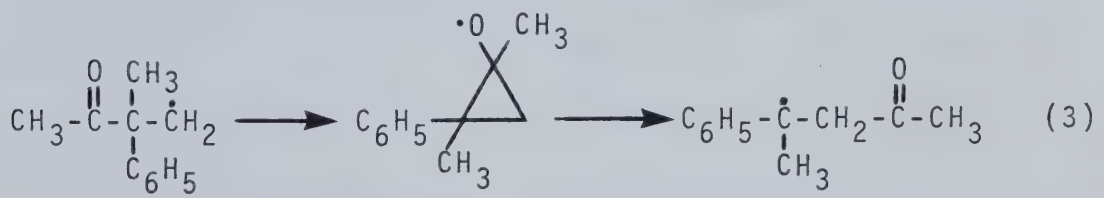
of the cyclohexylcarboxylate was rationalized by invoking a four-centered transition state (i), and the formation of gaseous products by a concerted pathway (ii), as shown in Scheme 8.



(SCHEME 8)

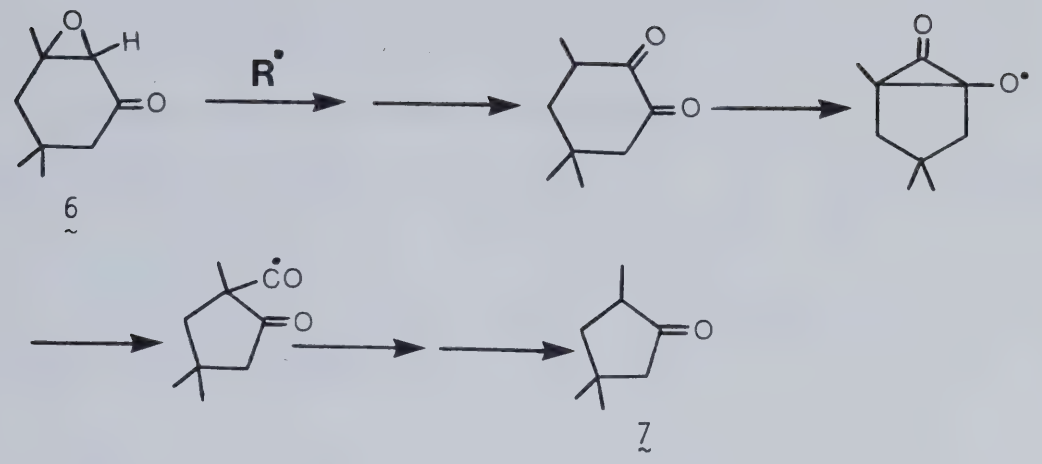
No evidence was given for such a proposal.

Considerable precedent may be found for the intramolecular radical addition to the carbonyl group. An example of such an addition is the facile 1,2-acetyl shift reported by Reusch.[13]



(3)

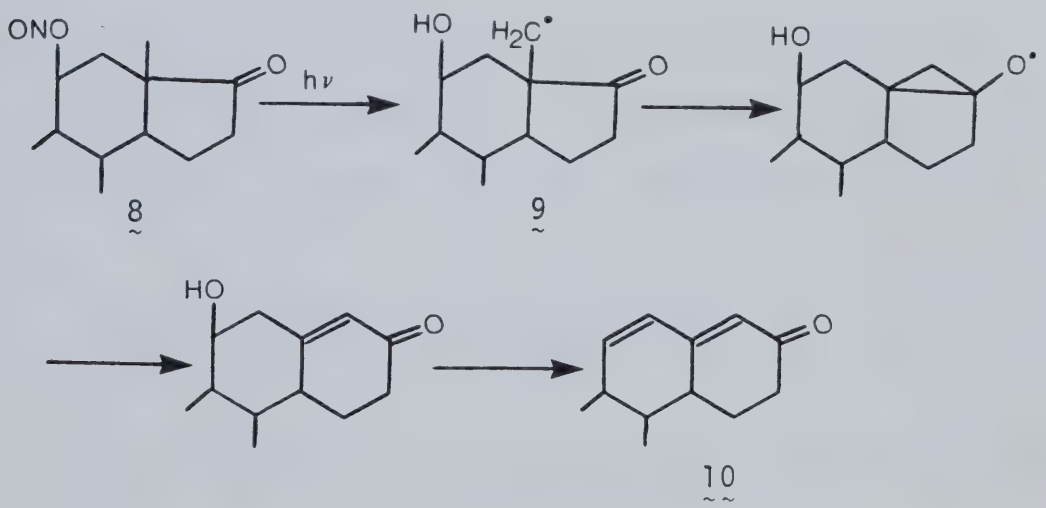
Reusch[14] also suggested an intramolecular acetylation in the radical catalyzed conversion of isophorone oxide (6) to 2,4,4-trimethylcyclopentanone (7), (Scheme 9).



6 7

(SCHEME 9)

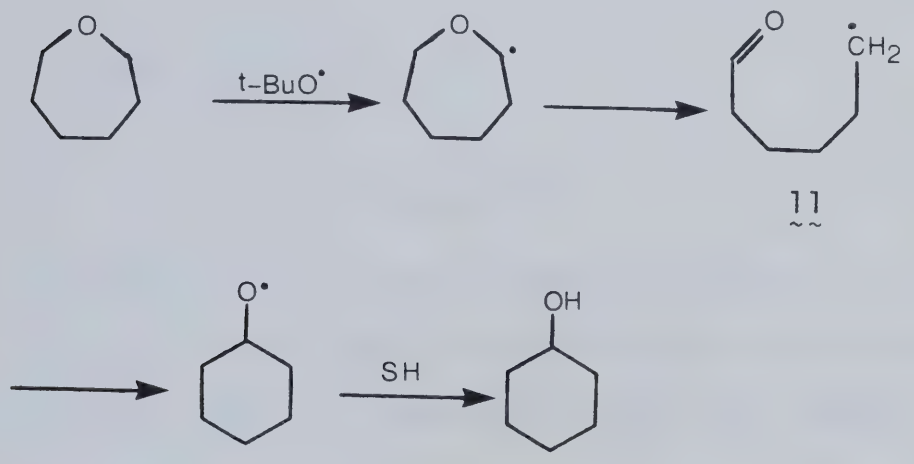
The conversion to the dienone (10) observed by Barton et al.[15] in the photolysis of the nitrite (8), (Scheme 10) can also be formally interpreted as proceeding by the addition of a carbon-free radical (9) to an unsaturated system, followed by fragmentation to form a carbonyl compound (10).



8 9 10

(SCHEME 10)

More recently Maillard[16] reported a new type of homolytic cyclization involving a carbonyl, and demonstrated that a 7-membered ring, oxepane, isomerizes to cyclohexanol in the presence of tert-butoxy radicals. The author proposed a radical mechanism in which the principle component is the intramolecular addition of an alkyl radical to the carbonyl group (Scheme 11).



11

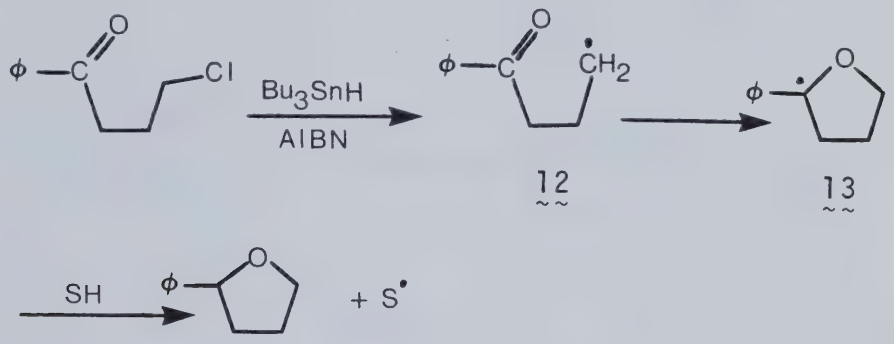
(SCHEME 11)

Radical (11) was generated independently from ω-halo-hexanal in the presence of tri-n-butyl stannane and AIBN. The radical was shown to produce cyclohexanol.

$$OHC\ (CH_2)_4\text{-}CH_2\text{-}X \xrightarrow[AIBN]{Bu_3SnH} 11 \qquad (4)$$

A number of examples of intramolecular radical additions to

oxygen of the carbonyl group have been reported. Thus the reduction of γ-chlorobutyrophenone by n-Bu_3SnH to yield 2-phenyltetrahydrofuran was reported by Kuivila,[17] (Scheme 12).

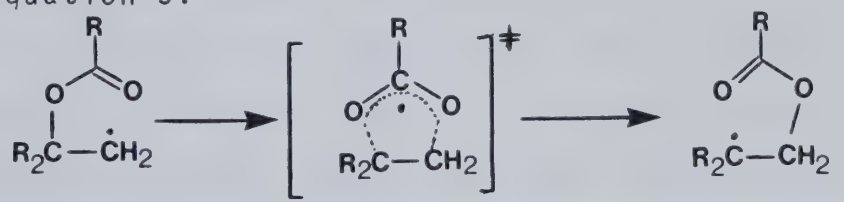


12 13

(SCHEME 12)

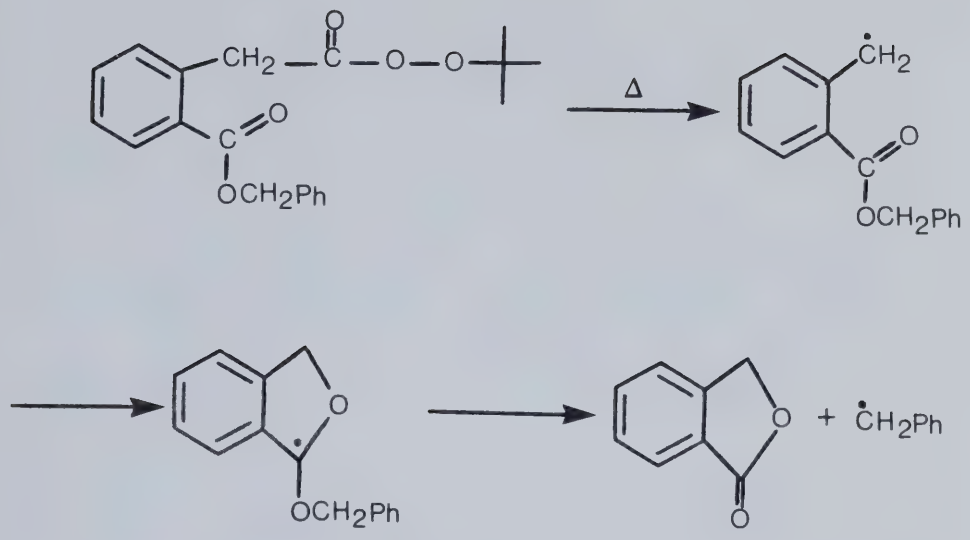
The initially formed carbon radical (12) adds intramolecularly to the oxygen of the carbonyl to produce radical (13) which is stabilized both by the benzene ring and the α-alkoxy group.

Intramolecular radical displacements on the carbonyl oxygen of ester groupings have also been observed. For example β-acyloxyalkyl radicals was shown to rearrange as shown in equation 5.[18]



(5)

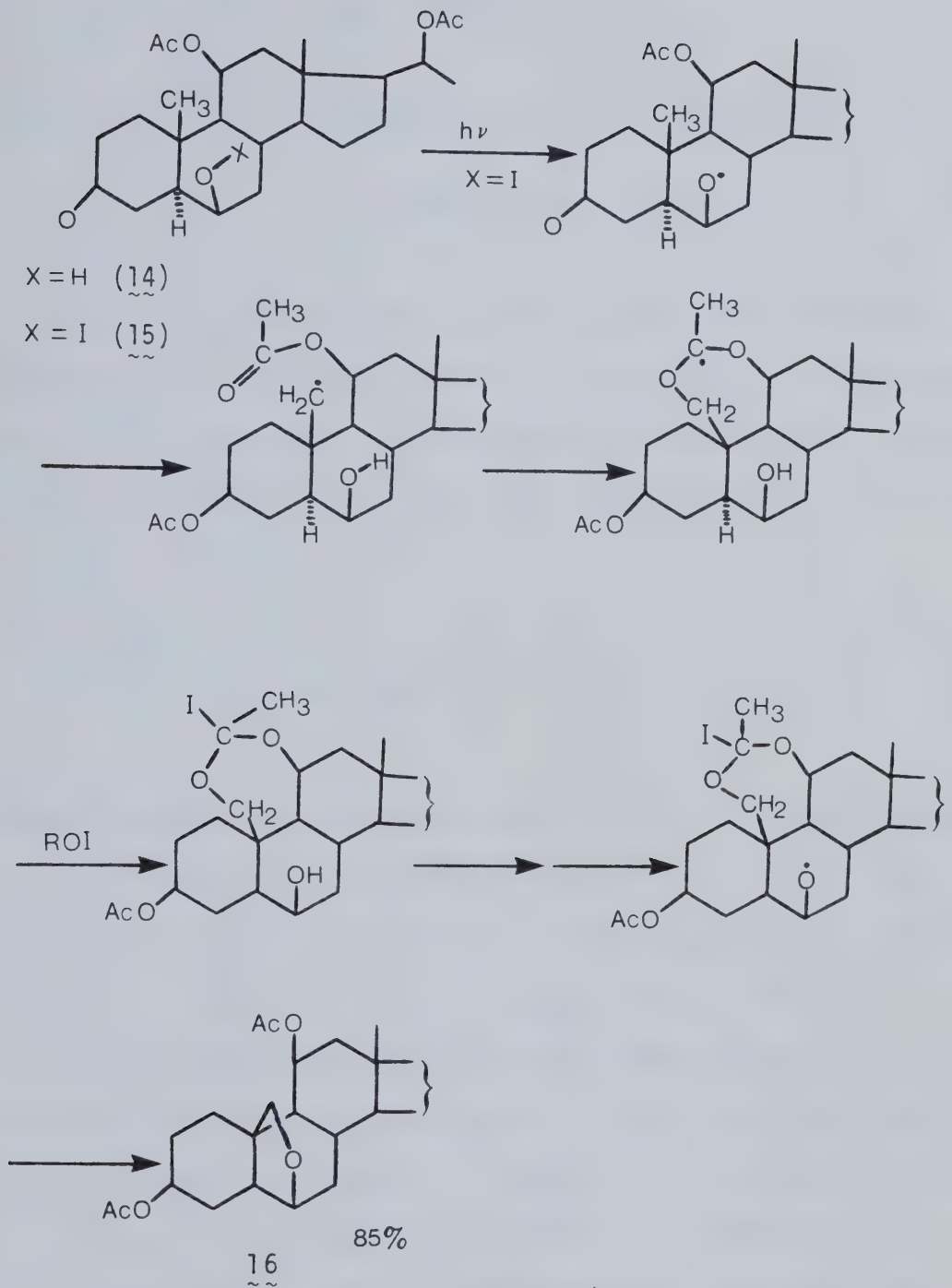
More recently, Tidwell[19] explained the formation of certain lactones by a radical displacement reaction on the carbonyl oxygen of the ester grouping (Scheme 13).



(SCHEME 13)

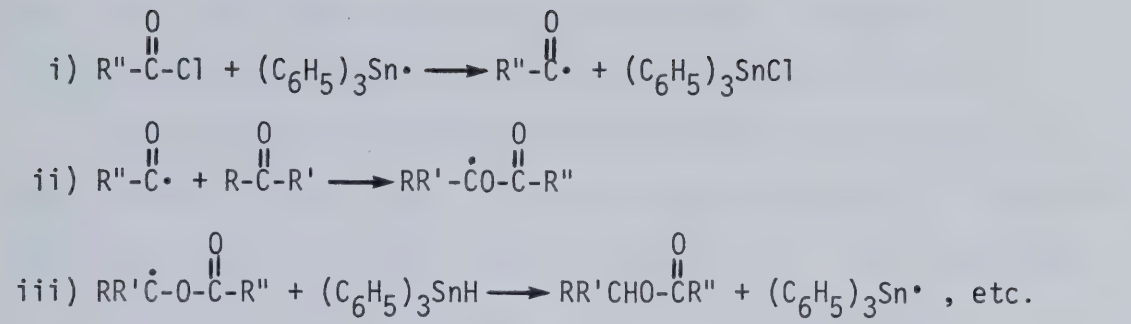
The intramolecular radical addition to the oxygen of the carbonyl group has been particularly useful in functionalization of unactivated carbon in steroids.[20] For example the hypoiodite reaction of 6β-hydroxy-11-β-acetoxysteroid(14), produced the 6β,19-ether (16) as the main product (Scheme 14).

There are no examples of intermolecular carbon centered radical attack on the oxygen of the carbonyl group, however there are a few reports of acyl radical attack on oxygen of ketones to produce esters.[21,22] Kaplan[21] used triphenyltin hydride and acyl chlorides to generate the acyl radicals, which subsequently reacted with a ketone in a chain reaction to give a quantitative yield of esters (Scheme 15).



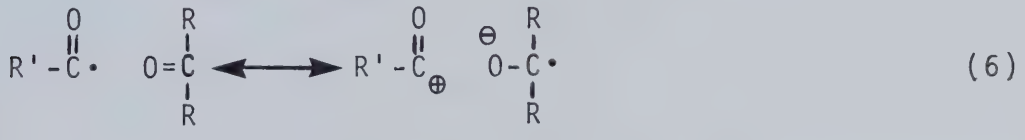
16

(SCHEME 14)



(SCHEME 15)

This reaction demonstrates a striking difference between acyl and alkyl radicals. Addition of the former to the oxygen atom of the carbonyl group probably involves stabilization of its transition state by the contribution of polar structures.[23]



(6)

These results suggest that the addition of acyl radicals is very rapid and probably irreversible, whereas the addition of alkyl radicals to carbonyl groups is reversible, as is the β-scission of tert-alkoxy radicals.[24]

Reactions involving intra and intermolecular free-radical addition to the cyanide triple bond have been demonstrated in a number of cases. The cyanation reactions of cyanogen chloride[2] and bromide[4] are examples of intermolecular addition-β-scission reactions, whereas the chain propagation steps proposed for the reactions of

alkyl radicals with cyanogen contained a sequence involving addition followed by hydrogen abstraction.[2]

Both inter and intramolecular radical additions to the cyanide triple bond to form an iminyl radical intermediate have been observed spectroscopically. The simplest imino radical, the methylene imino radical, $CH_2=N^{\cdot}$, produced by the addition of hydrogen atoms to hydrogen cyanide in a low temperature matrix, has been observed by esr spectroscopy.[25] The more recent examples of intermolecular free radical addition to cyanide are provided by Ingold.[26,27] Both diethoxyphosphonyl radicals, $(EtO)_2\dot{P}=O$, and trimethylsilyl radicals were allowed to react with tertiary butyl cyanide or acetonitrile in order to obtain the following unusually long-lived α-aminoalkyl radicals:

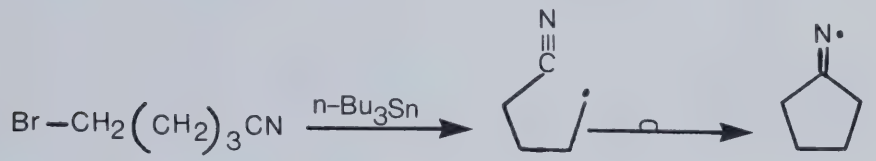
$$t\text{-Bu-C}\equiv\text{N} + 3\ (EtO)_2\dot{P}=O \longrightarrow t\text{-Bu-}\dot{C}(\text{-N}(P(O)(OEt)_2)_2)\text{-P}(O)(OEt)_2 \qquad (7)$$

$$t\text{-Bu-C}\equiv\text{N} + 4\ Me_3\dot{Si} \longrightarrow (Me_3Si)_2\dot{C}N(SiMe_3)_2 + t\text{-Bu}^{\cdot} \qquad (8)$$

$$CH_3\text{-C}\equiv\text{N} + 3\ Me_3\dot{Si} \longrightarrow CH_3(Me_3Si)\dot{C}N(SiMe_3)_2 \qquad (9)$$

Very few examples of intramolecular addition to cyanide can be found in the literature. Very recently Ingold[28] studied the rate of cyclization of 4-cyanobutyl

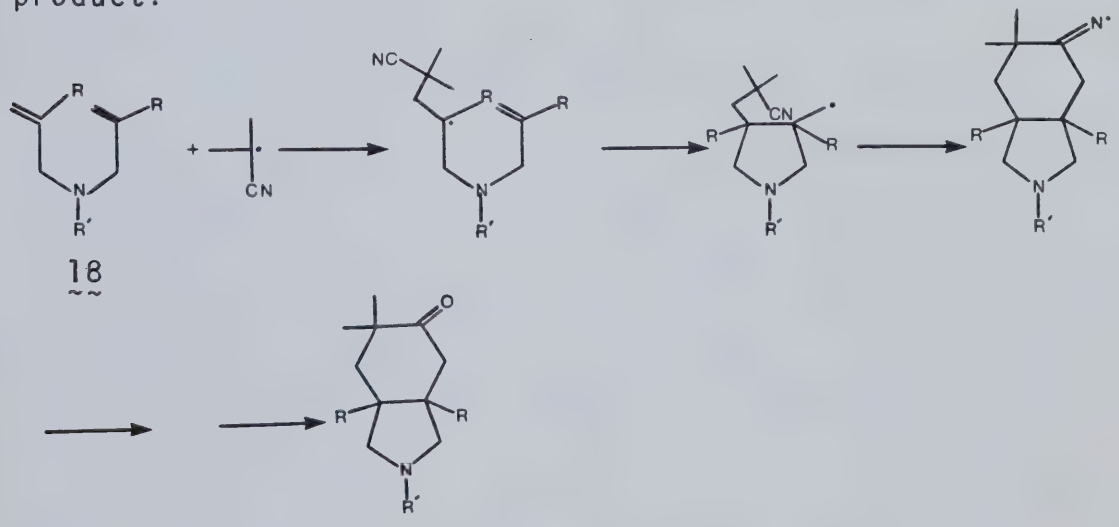
radicals (17), produced in the reaction of 5-bromovaleronitrile with tri-n-butyltin radicals, by epr spectroscopy and showed that this ring closure is somewhat slower than the analogous cyclization of the 5-hexenyl or the 5-hexynyl radical.



17

(10)

Intramolecular radical addition to a cyanide triple bond has also been observed in the azobisisobutyronitrile initiated polymerization of various N-substituted dialkylamines[29] (18), (Scheme 16). A low molecular weight compound which was identified as 6,6-dimethylperhydro-5-isoindolone (19) was formed. The following mechanism has been proposed for the formation of this product.



18

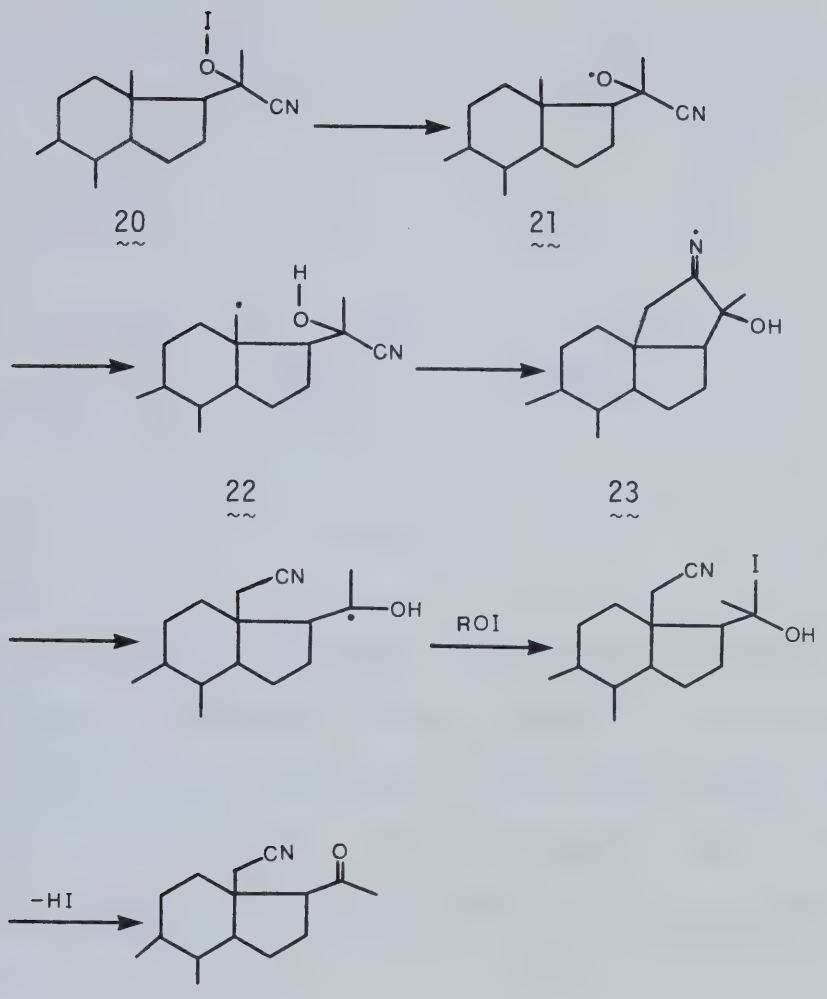
19

(SCHEME 16)

Synthetically useful methodology for the introduction of functionality at unactivated carbon-hydrogen bonds should combine a high degree of efficiency and regioselectivity. Various approaches to this problem relied on intramolecular free radical reactions to transfer a daughter functional group to a site distant from the parent functional group. This methodology has been applied in a few cases, for example, the intramolecular rearrangements occurring via an iminyl radical intermediate generated from the addition of an alkyl radical to an adjacent cyanide group have been reported by Heusler and Kalvoda.[19,30] The mechanism proposed to explain the products formed, suggested that an alkoxy radical (21), generated photochemically from the hypoiodite (20), abstracted an adjacent hydrogen in a six-membered ring transition state and that the intermediate iminyl radical (23) was formed via five-membered ring transition state (22), (Scheme 17).

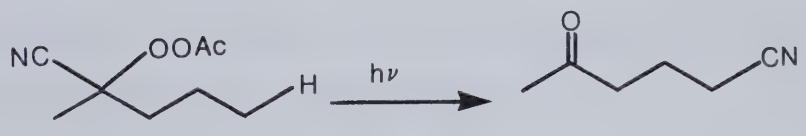
A similar reaction has recently been observed during the photolytic rearrangement of a number of α-peracetoxynitriles to ketonitriles,[31,32] (equation 11).

A mechanism consistent with the observed products involves (1) the homolysis of the oxygen-oxygen bond in the α-peracetoxynitrile (24), (2) δ-hydrogen atom abstraction, and (3) intramolecular cyano group transfer to the radical site in (26) to provide ultimately the



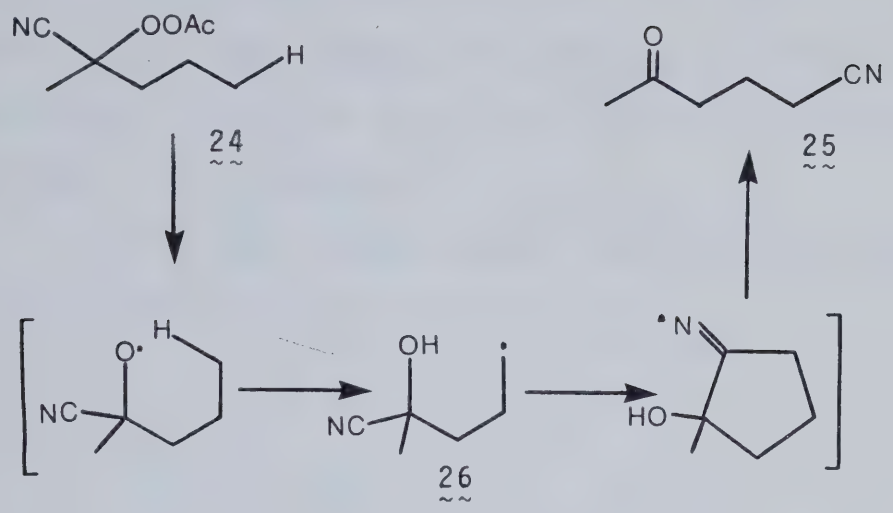
20 21 22 23

(SCHEME 17)



24 25 (11)

δ-ketonitrile (25), Scheme 18).



(SCHEME 18)

Proposal

The purpose of the work undertaken in the following report was to develop a method whereby a hydrocarbon, RH, could be functionalized via a cyanation reaction using a reagent, such as X-C≡N, in such a manner that a single product is obtained in high yield and with a high selectivity:

$$RH + XCN \longrightarrow RCN + HX \qquad (12)$$

As unactivated carbon can only be easily functionalized by a homolytic pathway, free radical processes were investigated for this cyanation reaction.

Since free radical addition to either cyanide or carbonyl had been separately reported for the reaction of different reagents, it was therefore of interest to investigate free radical additions to reagents which contain

both functionalities (-$\overset{O}{\overset{\|}{C}}$- and -CN). A synthetic method might be developed using such reagents to homologate an unactivated carbon by one or two carbon atoms depending upon the site of addition.

A few of the reagents which contain these two functionalities were chosen for initial study:

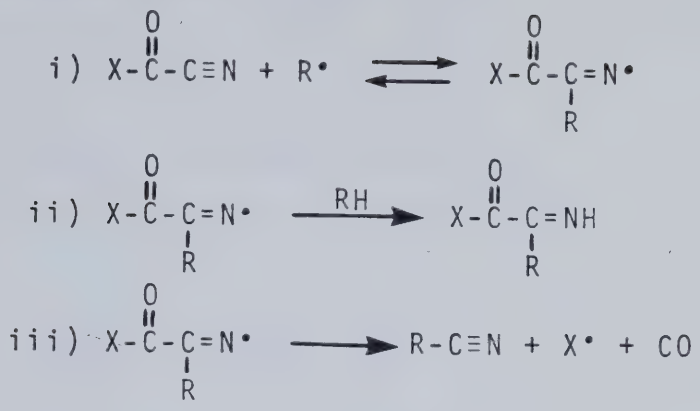
X-C≡N;

X = CH_3-O-$\overset{O}{\overset{\|}{C}}$, NC-$\overset{O}{\overset{\|}{C}}$, NC-$\overset{O}{\overset{\|}{C}}$-$\overset{O}{\overset{\|}{C}}$, CN.

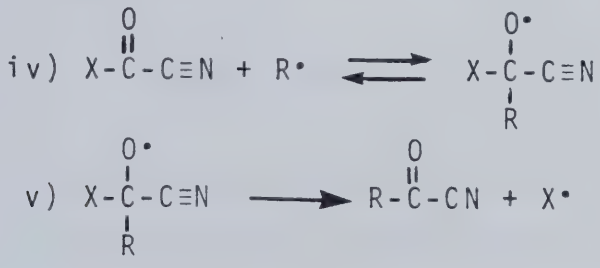
It was hoped that the radical addition to the cyanide and the subsequent β-scission would result in a new cyanation reaction (equations i-iii), or that the addition to carbonyl and subsequent β-scission would effect a selective functionalization of an unactivated carbon by a di-functionalized carbon moiety (equation iv-v). The latter process yields a product similar to that observed in the addition of a radical to cyanogen followed by hydrolysis,[2] (Scheme 19).

The reversibility of radical addition to carbonyl[5,8] and cyano[2,33] groups are well known processes.

cyanide addition:

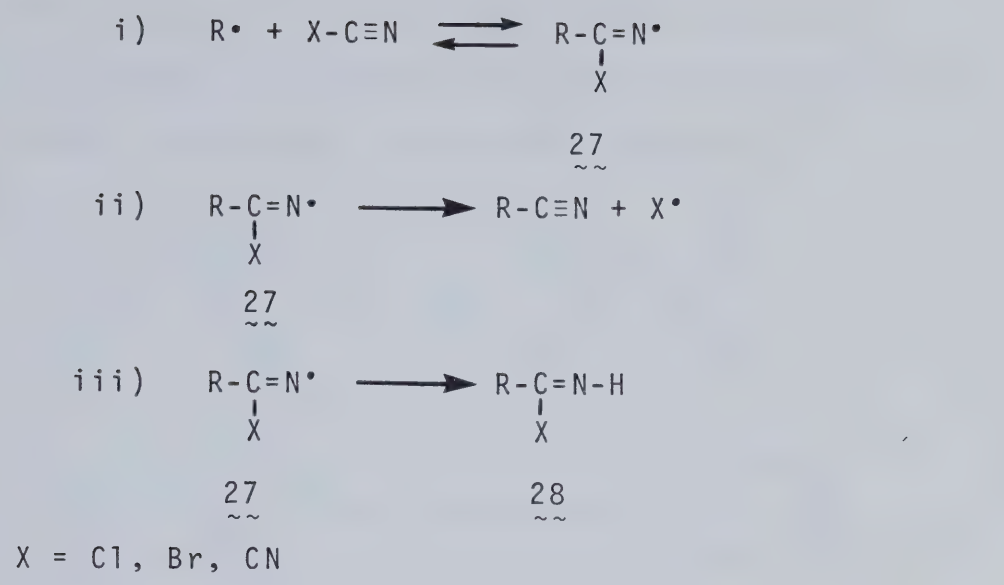


carbonyl addition:



(SCHEME 19)

The cyanation reaction of cyanogen halides and the reaction of 2,3-dimethylbutane with cyanogen have all been proposed to proceed via radical addition to cyanide. However, these reactions may also be reversible,[2] and this fact may possibly explain the failure of many hydrocarbons to react with cyanogen.

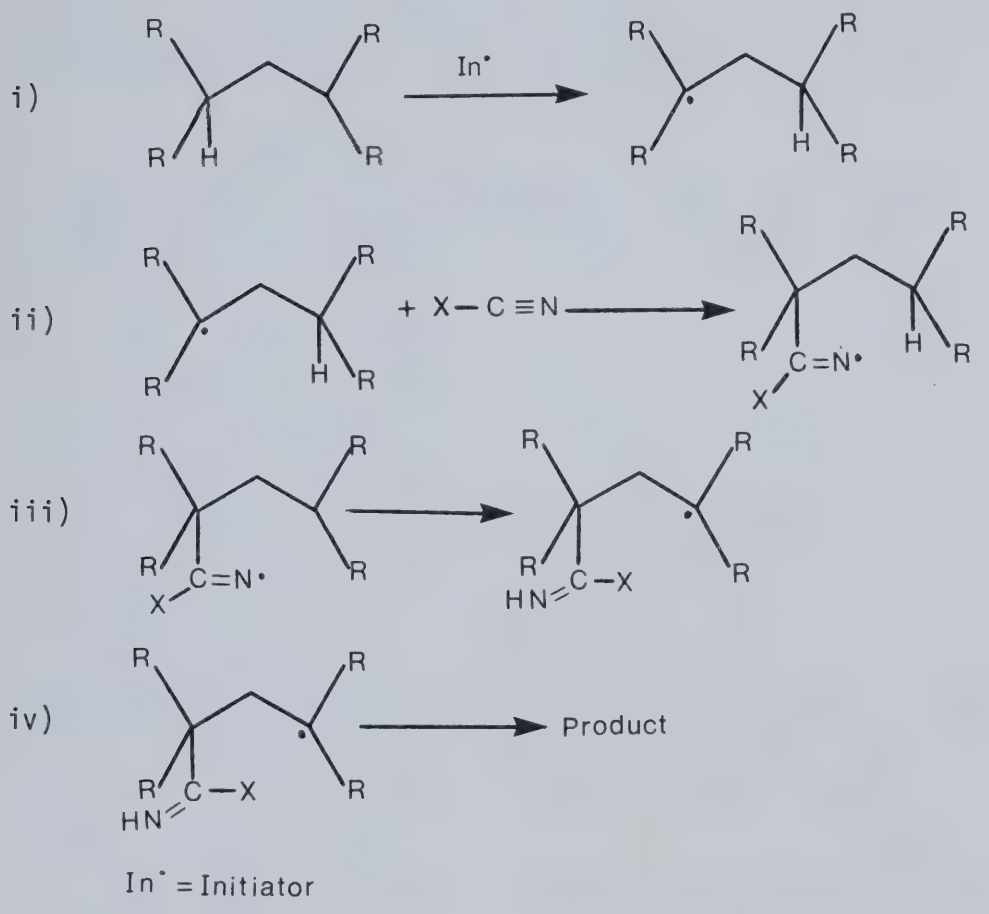


(SCHEME 20)

Depending on the nature of X, the iminyl radical intermediate (27) may undergo a β-scission to form alkyl cyanide and X•, which will carry the chain (equation ii). This is the case when X is a good leaving group and a good chain carrier (X = Cl, Br). However when X is not a good leaving group, the iminyl radical intermediate (27) abstracts a hydrogen to give the imine (28), (X = CN), (equation iii, Scheme 20).

It was thought that the selection of an appropriate hydrocarbon might enable the iminyl radical intermediate (27) to be trapped by intramolecular H-abstraction, and that the new radical formed would be appropriately positioned to add to the neighboring group, namely a carbonyl or a cyanide.

This type of transformation is particularly interesting since one would be able to difunctionalize an unactivated hydrocarbon in one step (Scheme 21).



(SCHEME 21)

In order to validate this hypothesis, 2,4-di-methylpentane was chosen as a hydrocarbon substrate (R = CH_3), and methyl cyanoformate or cyanogen as reagents (X = CN, $-\overset{O}{\overset{\|}{C}}-OCH_3$).

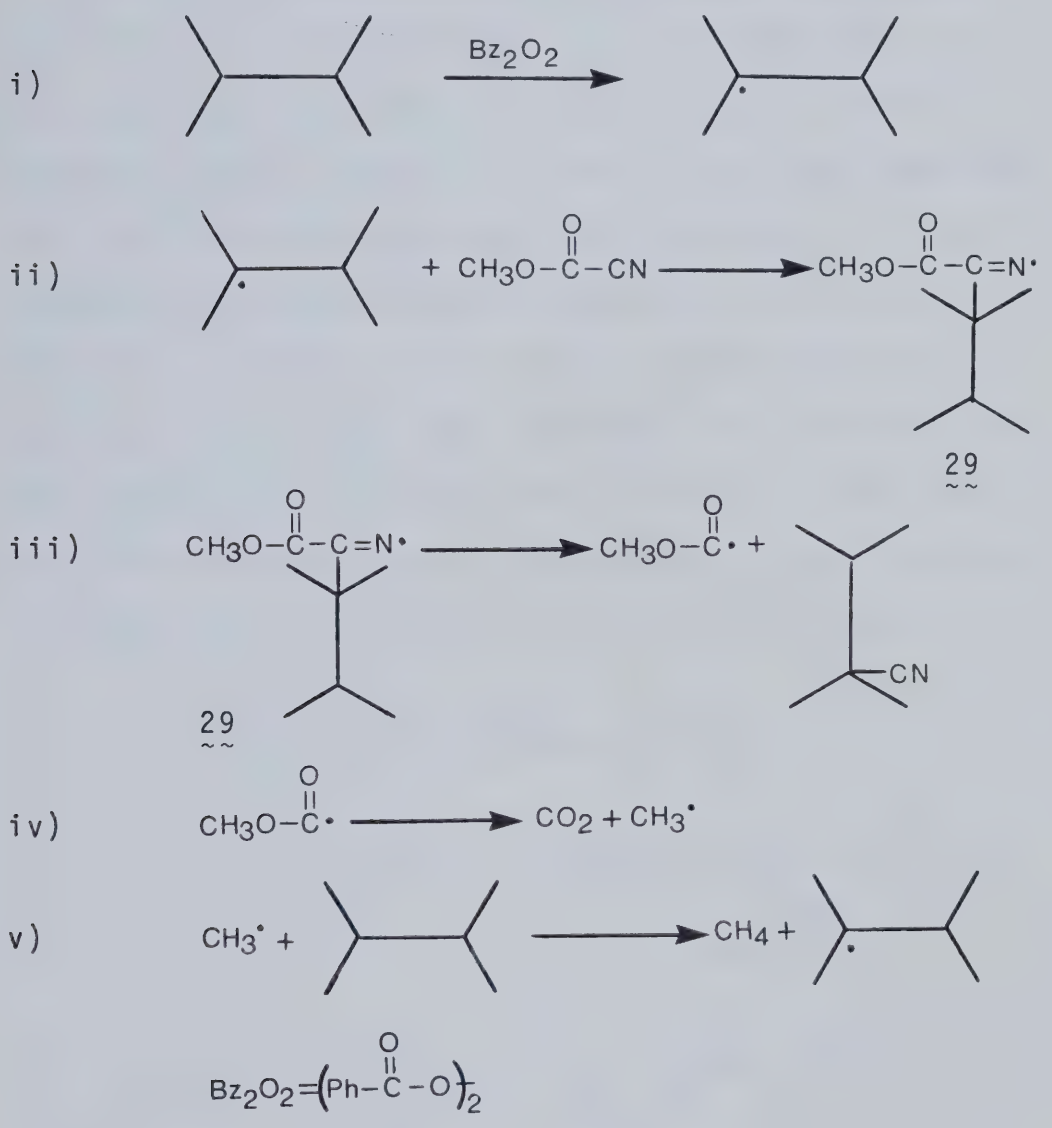
RESULTS AND DISCUSSION

Solutions of methyl cyanoformate (0.235 M) and benzoyl peroxide (10-24 mol %) in 2,3-dimethylbutane were heated in sealed, degassed reaction tubes at 99° for 5.5 h. One major product, α,α,β-trimethyl-butyronitrile (I), was detected (GLC) which resulted from the reaction of methyl cyanoformate and 2,3-dimethylbutane. The product appeared to be formed by a short chain process, since an optimum yield (77%) was obtained, at 89% conversion, when 24 mol% of benzoyl peroxide was used. Accompanying the cyanide, methane (35-40%) was isolated (Scheme 21). GLC-mass spectrometry of the reaction mixture showed the presence of a number of higher boiling minor products, two of which (3.7%) had a molecular formula of $C_9H_{15}O_2N$, and could be rationalized as 1:1 addition products of 2,3-dimethylbutane and methyl cyanoformate.

In the same manner, cyclohexane yielded cyclohexyl cyanide (72%) and methane (37-40%) when a 24 mol % of benzoyl peroxide was used. Cyclohexyl cyanide (35%) was likewise obtained using 10 mol % benzoyl peroxide.

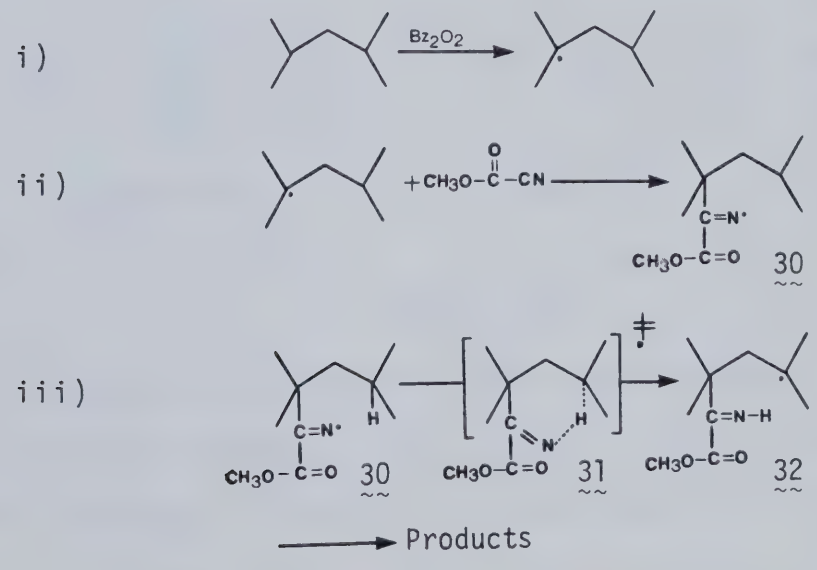
The reactions of the hydrocarbons, cyclohexane and 2,3-dimethylbutane, with methyl cyanoformate yielded products which could be rationalized by the addition of the radical to the cyanide triple bond, followed by

β-scission; no products derived from carbonyl addition were isolated, although in the case of the reaction of 2,3-dimethylbutane two minor products, $C_9H_{15}O_2N$ (3.7%), were detected (GLC-MS) which could conceivably be rationalized as carbonyl addition products.



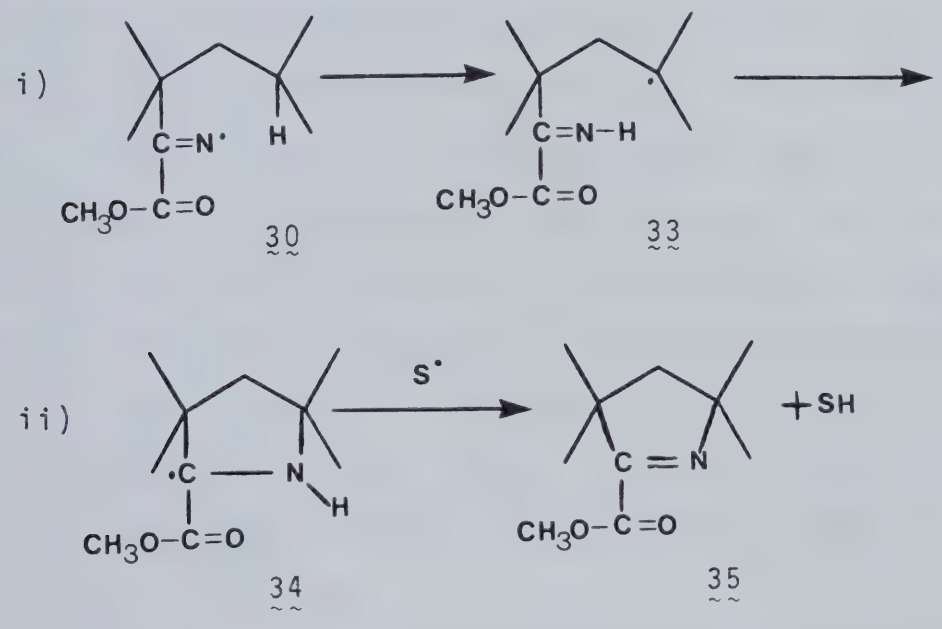
(SCHEME 22)

The cyanation reactions of the cyanogen halides and methyl cyanoformate and the reaction of 2,3-dimethylbutane with cyanogen[2] have all been proposed to proceed via radical addition to cyanide. In the latter reaction the iminyl radical formed, instead of undergoing a β-scission, abstracted a tertiary hydrogen to continue the chain. In an attempt to observe the combination of both addition and abstraction by the iminyl radical intermediate 29 (Scheme 22) proposed for the cyanation reactions of methylcyanoformate, the reaction of the reagent with 2,4-dimethylpentane was carried out. Since the reaction of 2,3-dimethylbutane with the reagent leads to addition followed by β-scission, it was hoped that if the tertiary hydrogen was made more favorably disposed toward abstraction, that intramolecular hydrogen abstraction could be observed (Scheme 23).



(SCHEME 23)

In accord with this prediction the reaction yielded 2,4-difunctionalized products. The reaction of methyl-cyanoformate (0.9 M) and benzoyl peroxide (50 mol %) in 2,4-dimethylpentane yielded, in addition to small amounts of primary (6%), secondary (12%), and tertiary (2%) cyanides, a heterocyclic ester, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene 35, (55%). The formation of the heterocyclic ester can be rationalized by a mechanism utilizing a unique but simple sequence of reactions which occur subsequent to the formation of the iminyl radical (30) (Scheme 24).



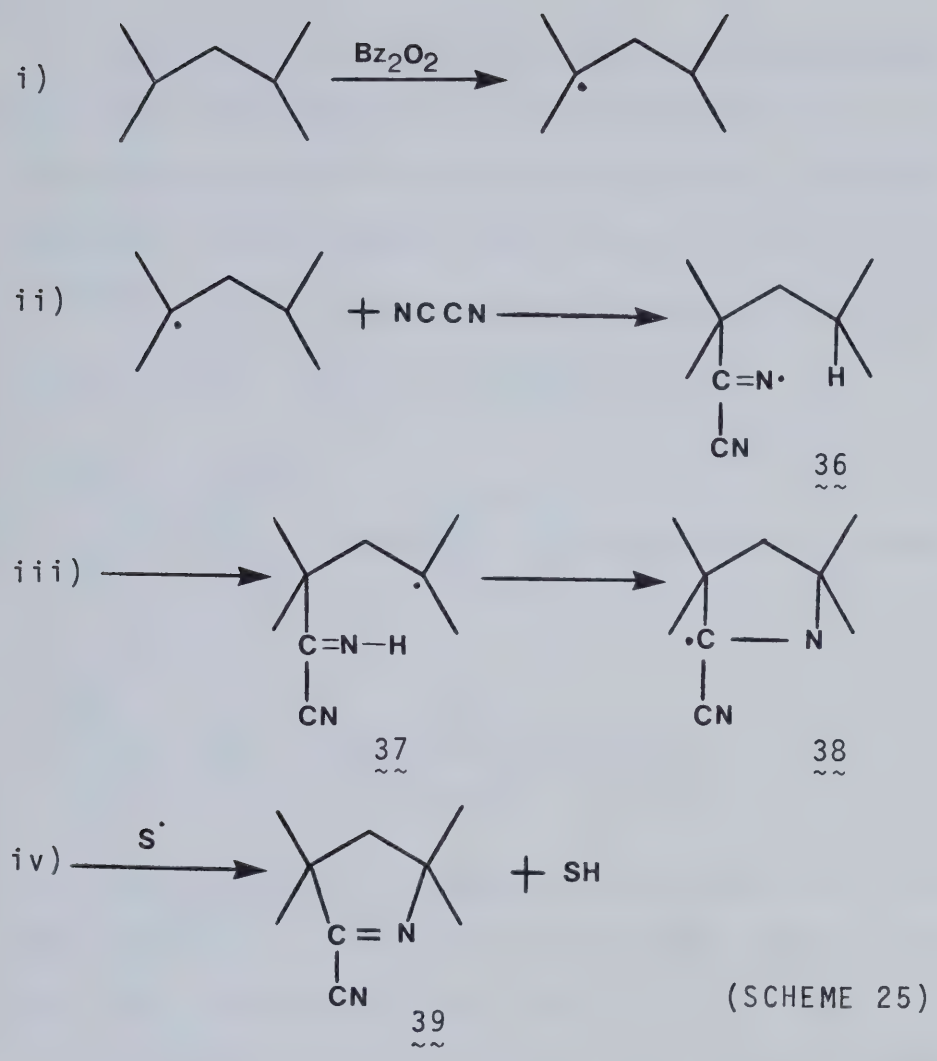
(SCHEME 24)

Internal abstraction by the iminyl radical forms a new tertiary radical (33), which is in position to add to the nitrogen of the imine double bond via a five-membered ring transition state. This step is similar to the

intramolecular radical addition to the oxygen of carbonyls[20] or esters.[19] The new carbon-centered radical (34), would be relatively stable, as it is adjacent to both the nitrogen and the ester carbonyl, and would eventually disproportionate to form the heterocycle 35.

Since a cyanide addition-abstraction sequence has been shown to proceed in the reactions of cyanogen with 2,3-dimethylbutane[2] and since the reaction of 2,4-dimethylpentane and methylcyanoformate is now proposed to proceed through a cyanide addition-internal abstraction followed by another internal addition, the reaction of cyanogen with 2,4-dimethylpentane might be expected to produce a 2,4-difunctionalized product in the same manner. The intermediate radical (37) would then be in a favorable steric arrangement to add internally to the adjacent imine via a five-membered ring transition state to form, as previously proposed, a carbon-centered radical which is stabilized by its adjacent groups, in this instance nitrogen and cyano groups. The stabilized radical (38) upon disproportionation would yield the cyclic product (39), (Scheme 25).

As predicted, when a mixture of 2,4-dimethylpentane (2 mL) and cyanogen (6.1×10^{-4} mol, 0.30 M) were allowed to react with benzoyl peroxide (105 mol %), a 22% yield of 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene (39) was

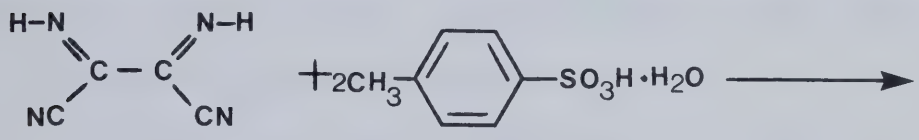


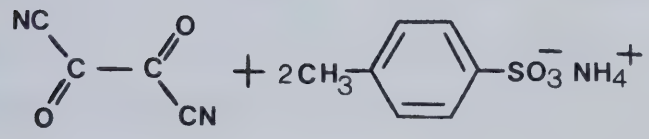
(SCHEME 25)

obtained. Since the disproportionation reaction is a chain-termination step, it is not surprising that a chain sequence was not observed and that only this modest yield was obtained.

In order to further investigate the orientation of the radical addition to bifunctional molecules and to establish the synthetic utility of these reactions, oxalyl cyanide and carbonyl cyanide were examined as possible cyanating or cyanocarbonylating agents.

The chemistry of oxalyl cyanide is relatively unexplored. This might be because of the very low yields obtained during the difficult preparation of this compound. Its synthesis was first reported by Begland[34] in 1972, and involved the partial hydrolysis of diiminosuccinonitrile (DISN) in acetonitrile.





The oxalyl cyanide is very moisture sensitive and rapidly hydrolyzes to oxalic acid and hydrogen cyanide if not kept under anhydrous conditions.

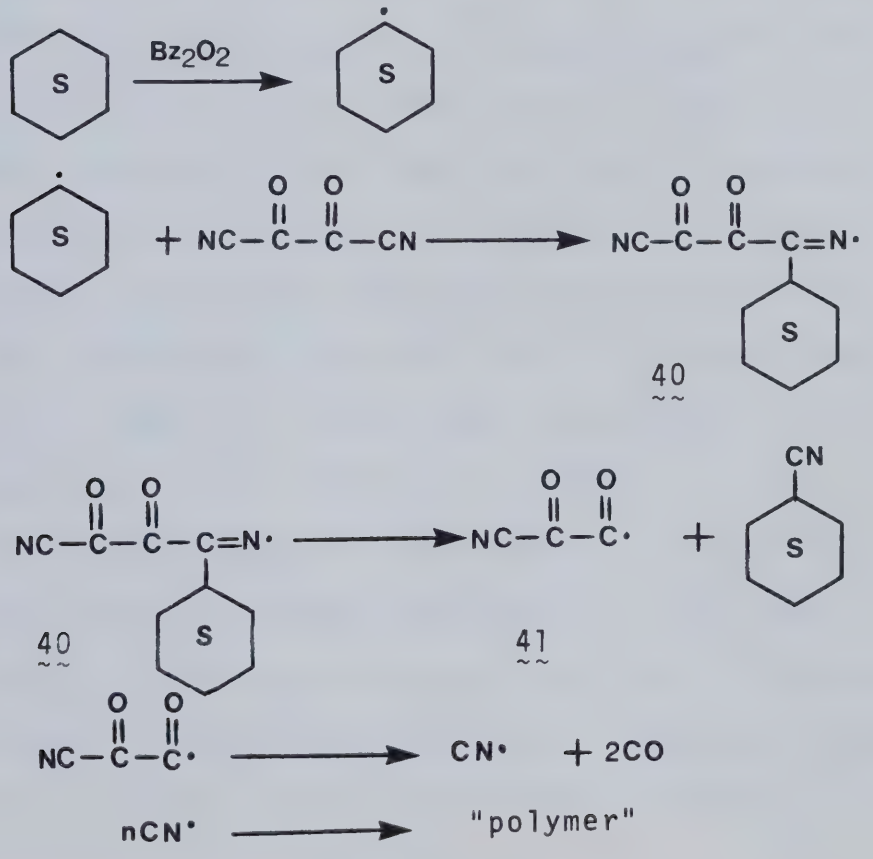
Solutions of oxalyl cyanide (0.245 M) and benzoyl peroxide (5-100 mol %) in cyclohexane were heated in sealed degassed reaction tubes at 90° for 9 h. The major reaction product was detected by GLC and characterized as cyclohexyl cyanide. The product appears to be formed by a nonchain process since an optimum yield of 40% was obtained when 100 mol % of benzoyl peroxide was used.

In the same manner, 2,3-dimethylbutane yielded only 1.5% of the expected tertiary cyanide, α,α,β-trimethyl-

butyronitrile, when 100 mol % benzoyl peroxide was used. No functionalized alkane was obtained when the reaction of oxalyl cyanide was carried out using 2,4-dimethylpentane as substrate. In all cases a dark brown residue was obtained, and was identified as a polymer, paracyanogen.

These preliminary results indicated that under these conditions oxalyl cyanide is not a good cyanating agent for hydrocarbons. However they do infer that attack at the nitrile group is preferred.

Although more work is required to establish a mechanism, it appears that the formation of cyclohexyl cyanide, in the reaction of oxalyl cyanide and cyclohexane, can be rationalized according to the following Scheme (26).



(SCHEME 26)

According to this mechanism, the cyclohexyl radical adds to the cyanide triple bond to form the iminyl radical intermediate (40), which then, through β-scission, produces cyclohexyl cyanide and the radical (41). Radical (41) further dissociates to form carbon monoxide and the cyanide radical. The cyanide radical subsequently polymerizes to give paracyanogen (Scheme 31).

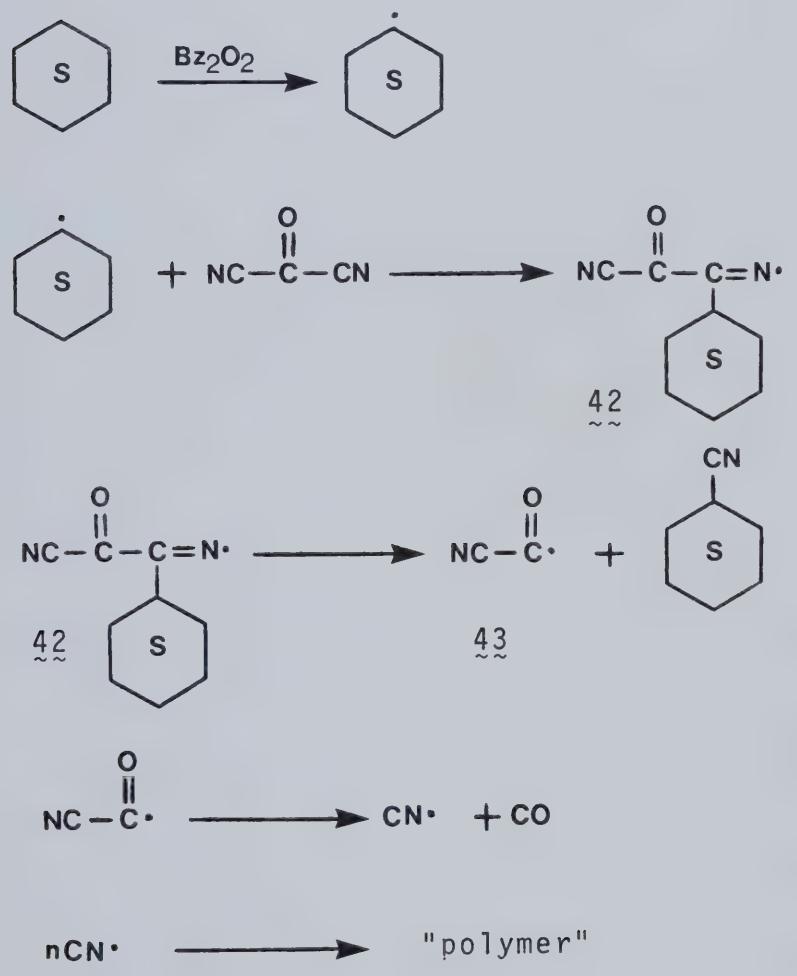
It has been shown[35] that irradiation of carbonyl cyanide at 2300-3500 Å results in dissociation to carbon monoxide and cyanide radicals. The cyanide radicals undergo polymerization. Similarly, at 750°, the vapor phase pyrolysis of carbonyl cyanide results in dissociation to carbon monoxide and cyanogen.[36]

The preliminary results indicated that the reaction of carbonyl cyanide with hydrocarbons is similar to that of oxalyl cyanide. Thus, when solutions of carbonyl cyanide (0.125 M) and benzoyl peroxide (5-200 mol %) were heated in sealed, degassed tubes at 90° for 6 h one major product was detected (GLC), resulting from the reaction of carbonyl cyanide and cyclohexane. The product was characterized as cyclohexyl cyanide.

The product appears to be formed in a nonchain process, since an optimum yield of 48.7% was obtained when 50 mol % of benzoyl peroxide was used. GLC-mass spectrometry of the reaction mixture showed the presence of benzoyl cyanide (<1%), whose yield increased by using

higher percentages of benzoyl peroxide (<3% using 200 mol % Bz_2O_2). However, when the reaction was tried with 2,3-dimethylbutane and 2,4-dimethylpentane, the cyanation reaction did not proceed to any appreciable extent, but again a dark brown precipitate, paracyanogen, was formed.

The formation of cyclohexyl cyanide can be rationalized according to the following Scheme (27).



(SCHEME 27)

According to this mechanism, the cyclohexyl radical adds to the cyanide triple bond to form the iminyl radical intermediate (42), which then, through β-scission, produces cyclohexyl cyanide and the radical (43). Radical (43) further dissociates to form carbon monoxide and the cyanide radical. The cyanide radical subsequently polymerizes to give paracyanogen (Scheme 27).

EXPERIMENTAL

Materials

The hydrocarbons 2,3-dimethylbutane (>99.8%), 2,4-dimethylpentane (>99.7%), and cyclohexane (99.5%, Phillips research grade) were used without further purification. Tetracyanoethylene (98%, Aldrich) was used without further purification.

Methyl cyanoformate was prepared according to the method of Childs and Weber[37] in 43% yield, bp. 92-94°C (690 mm) [Lit.[37] bp. 95-96°C (760 mm), in 76% yield]; n_D^{25} 1.3712. The IR and NMR spectra were identical with those reported.

Cyanogen and hydrogen cyanide (Matheson Co., Inc.) were distilled before use. Diiminosuccinonitrile, the starting material for the preparation of oxalylcyanide, was prepared according to the method of Begland et al.[38] in 87% yield: m.p. 168-170°C [Lit.[38] m.p. 165-166°C]. The oxalyl cyanide, which was obtained by the partial hydrolysis of diiminosuccinonitrile (4.6%), was sublimed 3 times at 50°C and 0.5 mm. m.p. 60-61°C (Lit.[38] m.p. 61-62°), IR (CH_2Cl_2) 2230 cm^{-1} (C≡N) and ν 1735 cm^{-1} (C=O).

Carbonyl cyanide was prepared by Benson's method,[39] by the reduction of tetracyanoethylene oxide using n-Bu_2S, in 50% yield, bp. 61-62°C at 700 mm, (Lit.[39]

65.6°C at 760 mm Hg); IR (CH_2Cl_2) ν 2240 cm^{-1} (C≡N), ν 1720 cm^{-1} (C=O). The precursor of carbonyl cyanide, tetracyanoethylene oxide, was prepared as colorless needles in 50% yield by the oxidation of tetracyanoethylene using 30% hydrogen peroxide, m.p. 178-180°C (Lit.[38] 177-178°C), IR (CH_2Cl_2) ν 2270 cm^{-1}.

Reaction of Methyl Cyanoformate with 2,3-Dimethylbutane.

A mixture of methyl cyanoformate (200 mg, 2.35 mmol) and benzoyl peroxide (137 mg, 0.566 mmol) in 2,3-dimethylbutane (10 mL, 77 mol) was placed in a Pyrex ampule, degassed, and thermostated at 99°C for 5.5 h. The reaction mixture was subjected to GLC analysis (8 ft. x 1/8 in., 5% UCON polar, 50 HB, 2000 on Chromosorb W, 45-200°C). The analysis showed three major fractions: a low boiling fraction containing 2,3-dimethylbutane, benzene, and unreacted methyl cyanoformate (11%); a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction was isolated by preparative GLC and shown to be α,α,β-trimethylbutyronitrile (77%). The structure of the nitrile was assigned by a comparison of its IR and NMR spectrum with those of an authentic sample.

Methane was fractionated, measured using a Toepler pump by conventional vacuum line techniques,[40] and was

identified and its purity checked by comparing its GLC retention time and mass spectrum with those of an authentic sample.

In order to obtain an optimum yield of the nitrile, reactions were run under the above conditions using varying amounts of benzoyl peroxide (10-96 mol %):

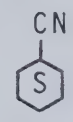
Bz_2O_2 mol %	% Yield
10	46
12	54
24	77
96	53

Reaction of Methyl Cyanoformate with Cyclohexane.

A mixture of methyl cyanoformate (200 mg, 2.35 mmol) and benzoyl peroxide (137 mg, 0.5 mmol) in cyclohexane (10 mL, 93 mmol) was placed in a Pyrex ampule, degassed and sealed, and the reaction was carried out and analyzed as was the reaction using 2,3-dimethylbutane. GLC analysis showed three major fractions: a low boiling fraction containing cyclohexane, benzene, and unreacted methyl cyanoformate (7%); a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction from this reaction was a single compounent, cyclohexyl cyanide (72%). The product was collected by preparative GLC and its structure was assigned by a comparison of

its GLC retention time, IR and NMR spectrum with those of an authentic sample.

In order to obtain an optimum yield of the nitrile, reactions were run under the above conditions using varying amounts of benzoyl peroxide (10-105 mol %):

Bz_2O_2 mol %	 % Yield
10	35
24	72
85	50
105	44

Reaction of Methyl Cyanoformate with 2,4-Dimethylpentane.

A mixture of methyl cyanoformate (114 mg, 1.34 mmol) and benzoyl peroxide (654 mg, 2.70 mmol) in 2,4-dimethylpentane (2 mL, 13.4 mmol) was placed in a Pyrex ampule, degassed, and sealed. The ampule was thermostated at 99°C for 9 h. The reaction vessel was opened and the mixture was analyzed by GLC (8 ft. x 1/8 in., 7% SE-30 on Chromosorb W, 110°C). The analysis showed three major fraction. A low-boiling fraction containing unreacted 2,4-dimethylpentane, methyl cyanoformate, benzene, and three other compounds identified as 2,2,4-trimethylpentanonitrile (2%), 2-isopropylisopentanonitrile (12%), and 3,5-dimethylhexanonitrile (6%) (in order of their elution). The middle fraction was composed of a single

compound, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene (55%). The high boiling fraction contained a large number of compounds which were not identified.

The three cyanides (primary/secondary/tertiary) were collected as a mixture by preparative GLC (10 ft. x 1/4 in., 10% SE-30 on Chromosorb W). An elemental analysis of this sample showed it to be an isomeric mixture of the three nitriles. Anal. Calcd for $C_8H_{15}N$: C, 76.45; H, 12.07; N, 11.18. Found: C, 76.75; H, 12.23; N, 10.94. The mixture was separated and the three nitriles collected by preparative GLC. Their structures were assigned on the basis of their IR and NMR spectra.

2,2,4-Trimethylpentanonitrile: NMR ($CDCl_3$) δ 1.02 (d, J = 6 Hz, 6H), 1.36 (s, 6H), 1.42 (d, J = 6 Hz, 2H), 1.82 (m, J = 6 Hz, 7H); IR (CH_2Cl_2) ν 2230 cm^{-1} (C≡N).

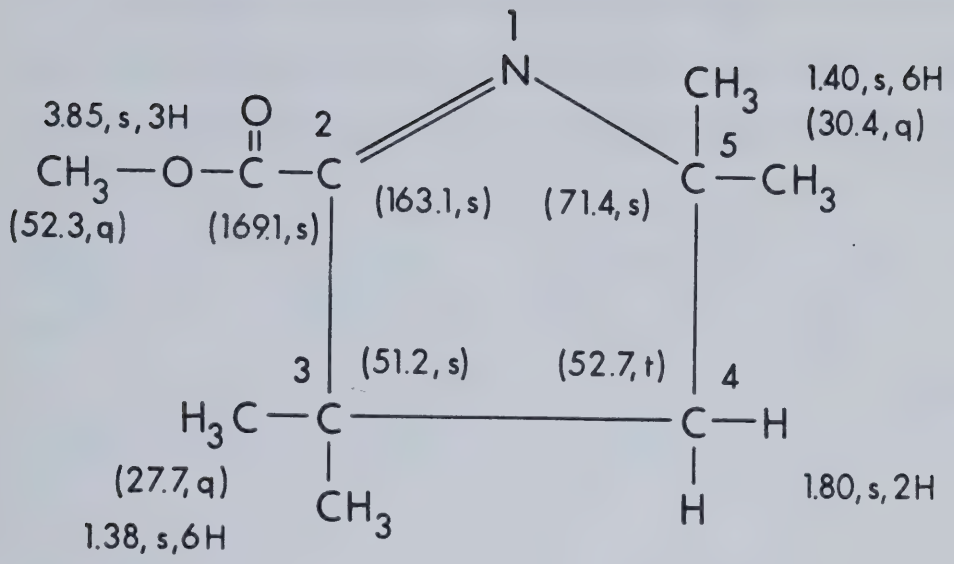
2-Isopropylisopentanonitrile: NMR ($CDCl_3$) δ 1.0 (d, J = 6 Hz, 6H), 1.06 (d, J = 6 Hz, 6H), 1.92 (m, J = 6 Hz, 3H); IR ($CHCl_3$) ν 2220 cm^{-1} (C≡N).

3,5-Dimethylhexanonitrile: IR ($CHCl_3$) ν 2225 cm^{-1}. The NMR sample appeared to be admixed with the other isomers and the spectrum could not be analyzed, although it was consistent with the assigned structure. However, the microanalysis of the mixture and the identification of the other two possible isomers allowed its assignment.

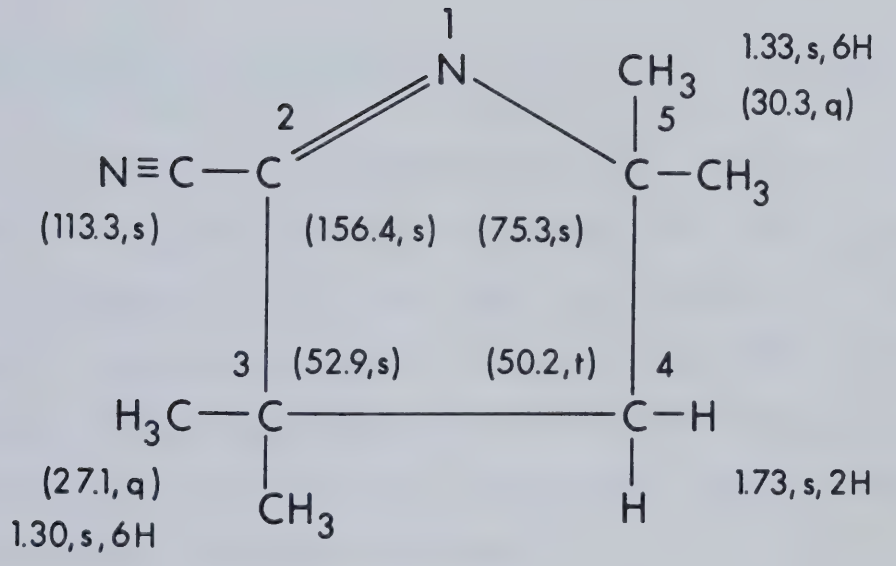
The structure of 2-carbomethoxy-3,3,5,5-tetramethyl-azacyclopent-1-ene, collected by preparative GLC (SE-30 column), was assigned on the basis of its microanalysis,

its mass spectrum, and its IR and NMR (^{13}C and ^{1}H) spectrum: IR (CH_2Cl_2) ν 1735 cm^{-1} ($-CO_2CH_3$), 1622 cm^{-1} (-C=N-); mass spectrum m/e 183 (M^+, 11.9%), 168 (M^+-15, 63.5%), 127 (M^+-56.24%), 124 (M^+-59, 19.1%), 42 (M^+-141, 100%); NMR ($CDCl_3$) chemical shifts, multiplicity, and assignments are given in Figure 1 for both the ^{1}H and ^{13}C spectrum. Anal. calcd for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.28. Found: C, 65.46; H, 9.20.

The mass spectrum and elemental analysis of 35 clearly established its molecular formula to be $C_{10}H_{17}NO_2$. The ^{1}H NMR showed two sets of chemically nonequivalent methyl groups, one pair of methylene protons, and one set of protons assignable to the absorption for a methyl ester. The ^{13}C NMR and IR spectra allow the assignment of the structure given in Figure 1. The chemical shift of the ester carbonyl (169.1 ppm) agrees with its IR absorption (1735 cm^{-1}), while the C-2 absorption can only be a doubly bonded carbon and is in agreement with its assignment as an iminyl carbon whose IR absorption appears at 1622 cm^{-1}. The C-4 ^{13}C chemical shift is that of a methylene group flanked by two tertiary carbon atoms, and its absorption was inconsistance with any other structural arrangement that could be drawn. With these partial structural features the only structure that can be assigned for 35 was 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene.



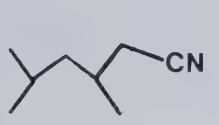
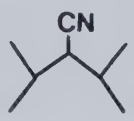
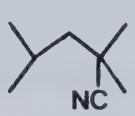
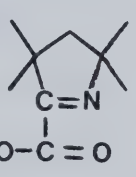
35



39

Figure 1. NMR spectral assignments of compound (35) and (39). Chemical shifts and multiplicities for ^{1}H spectra δ downfield from Me_4Si, ^{13}C spectral assignments (parenthesis) ppm downfield from Me_4Si.

In order to obtain an optimum yield of the products, reactions were run under the above conditions using varying amounts of benzoyl peroxide (24-200 mol %):

Bz_2O_2 mol %				
	% yield			
24	3	6.6	1.1	25
50	6	12	2	55
100	5	11	1.6	50
150	6	14	2	53
200	5.5	12	1.6	44

The Reaction of 2,4-Dimethylpentane with Cyanogen.

A mixture of cyanogen (0.61 mmol, 0.305 M) and benzoyl peroxide (155 mg, 0.64 mmol, 0.32 M) in 2,4-dimethylpentane (2 mL, 13.4 mmol) was placed in a Pyrex ampule, degassed, sealed, and heated at 98°C for 3 h. After heating, the reaction ampule contained a light brown supernatant solution and a dark brown polymeric material (presumably polymeric cyanogen[41]).

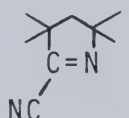
Analysis of the supernatant liquid by GLC (8 ft. x 1/8 in., 7% SE-30 on Chromosorb W, 90°) showed three major fractions: a low boiling fraction containing unreacted 2,4-dimethylpentane and benzene (identical GLC

retention times with those of the authentic materials), a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction was isolated by preparative GLC (SE-30 column) and shown to be 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene (22%). The structure of this compound was assigned on the basis of its IR, NMR (^{1}H and ^{13}C) and mass spectrum, and its elemental analysis: IR (CH_2Cl_2) ν 2240 (-C≡N, very weak), 1620 cm^{-1} (-C=N-). NMR ($CDCl_3$), see Figure 1 for the ^{1}H and ^{13}C spectral assignments. The mass spectrum of 41 showed M^+, M^+-1, M^+-15 peaks: m/e 150.1152 (8.4%), calculated for $C_9H_4N_2^+$, 150.1157; 149.1075 (5.5%), calculated for $C_9H_{13}N_2^+$, 149.1079; 135.0923 (100%), calculated for $C_8H_{11}N_2^+$, 135.0922. Anal. calcd for $C_9H_{14}N_2$: C, 71.95; H, 9.39. Found: C, 71.72; H, 9.30.

The mass spectrum and elemental analysis of (39) clearly established its molecular formula to be $C_9H_{14}N_2$. The ^{1}H NMR shows that there are two sets of chemically nonequivalent methyl groups and one pair of methylene protons. The ^{13}C NMR and IR spectra along with the above information allows the assignment of the structure given in Figure 2. The chemical shift of the nitrile carbon (113.3 ppm) agrees with its IR absorption (2240 cm^{-1}), while the remaining nitrogen double bonded to carbon C-2 influences the chemical shift of that carbon to appear

at 156.4 ppm. The IR absorption of the iminyl group at 1620 cm^{-1} supports this structural assignment. The C_4 ^{13}C chemical shift is that of a methylene group flanked by two tertiary carbon atoms and its absorption was inconsistent with any other structural arrangement that could be drawn. With these partial structural features the only structure that can be assigned for (39) was 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene.

In order to obtain an optimum yield of the dinitrile, reactions were run under the above conditions using varying amounts of benzoyl peroxide (30-155 mol %):

Bz_2O_2 mol %	 % Yield
30	7.4
62	16.8
93	18.3
124	21
150	22.3

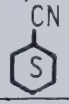
Reaction of Carbonyl Cyanide with Cyclohexane.

A mixture of carbonyl cyanide (10 mg, 0.125 mmol) and benzoyl peroxide (15 mg, 0.0625 mmol) in cyclohexane (1 mL, 9.3 mmol) was placed in a Pyrex ampule, degassed, sealed and heated at 95° for 9 h. The reaction mixture

was subjected to GLC analysis (8 ft., 1/8 in., 7% SE-30 on Chromosorb W, 60-180°, and 10 ft., 1/8 in., 10% UCON polar, 50 HB, 2000 on Chromosorb W, 60-180°). The analysis showed three major fractions; a low boiling fraction containing cyclohexane and benzene, a middle fraction containing the major compound, cyclohexyl cyanide (48.7% based on a 100% conversion). The cyclohexyl cyanide was identified by GC/MS and a comparison of its GLC retention time with those of an authentic sample. The middle fraction also contained benzoyl cyanide (<1%) which was tentatively identified by comparison of its GLC retention time with that of an authentic sample. The high boiling fraction contained a large number of compounds which were not identified.

A dark brown residue was obtained in this reaction which was identified by its IR spectrum (CH_2Cl_2) ν 1570 cm^{-1} as paracyanogen.[42] No attempt was made to analyze the gaseous product(s).

In order to obtain an optimum yield of cyclohexyl cyanide, reactions were run under the above conditions using varying amounts of benzoyl peroxide (5-100 mol %):

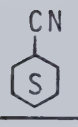
Bz_2O_2 mol %	 Yield %
5	0
20	17.5
50	48.7
100	44.5

Reaction of Oxalyl Cyanide with Cyclohexane.

A mixture of oxalyl cyanide (62 mg, 0.574 mmol) and benzoyl peroxide (139 mg, 0.574 mmol) in cyclohexane (3 mL, 27.8 mmol) was placed in a Pyrex ampule, degassed and thermostated at 90° for 9 h. The reaction mixture was subjected to glpc analysis (8 ft. x 1/8 in., 5% UCON polar, 50 HB, 2000 on Chromosorb W, 45-200°). The analysis showed three major fractions: a low boiling fraction containing cyclohexane and benzene, a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction was isolated by preparative GLC and shown to be cyclohexyl cyanide (40%). The structure of the cyanide was assigned by a comparison of its IR, NMR spectrum, and GLC retention time with those of an authentic sample.[4]

In each run, a dark brown polymeric material was obtained whose IR spectrum, (CH_2Cl_2) ν 1570 cm^{-1}, showed it to be paracyanogen.[47] No attempt was made to measure any gaseous product(s) nor to recover any oxalyl cyanide that might not have been reacted.

In order to obtain an optimum yield of cyclohexyl cyanide, reactions were run under the above conditions using varying amounts of benzoyl peroxide (5-100 mol %):

Bz_2O_2 mol %	 Yield %
5	0
20	1.7
40	14
60	22
100	40

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were determined on a Varian HA-100 spectrometer fitted with a Digilab FTS/NMR-3 data system

The ^{13}C NMR spectra were determined on natural abundance samples at 22.628 MHz (Bruker HFX-90) or at 15.08 MHz (Brucker WP-60) in 10-mm sample tubes. $Cr(acac)_3$ was added to reduce the relatively long relaxation time of the -C≡N carbon.

Mass Spectra. Mass spectra were determined using an AEI MS-12 mass spectrometer attached to a gas chromatograph (Varian 1400), and coupled to a computer data system (Nova-3) with program DS-50. The high resolution mass spectra were obtained using an AEI MS-50 mass spectrograph (70 eV), which was likewise coupled to the Nova-3 data handling computer.

GLC Analysis. The GLC analyses were carried out using a HP-4850 equipped with a thermal conductivity detector and

electronic integrator, or using a Varian 1520 also equipped with a thermal conductivity detector which was attached to a HP-3380 A integrator. All quantitative values were calculated using standard calibration curves determined using known mixtures of the authentic materials, except for 3,5-dimethylhexanonitrile, 2-isopropylisopentanonitrile, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene and 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene where the calibration factor of one was assumed. Heptane, nonane, undecane and dodecane were used as external standards.

REFERENCES

1. E. Müller and H. Huber, Chem. Ber., 96, 670 (1963).
2. D.D. Tanner and N.J. Bunce, J. Amer. Chem. Soc., 91, 3028 (1969).
3. N.J. Bunce and D.D. Tanner, J. Amer. Chem. Soc., 91, 6096 (1969).
4. D.D. Tanner, G. Lycan, and N.J. Bunce, Can. J. Chem., 48, 1492 (1970).
5. W.G. Bentrude and K.R. Darnall, J. Amer. Chem. Soc., 90, 3588 (1968).
6. D.D. Tanner and N.C. Das, J. Org. Chem. 35, 3972 (1972).
7. T.S. Oakwood and C.A. Weisgerber, "Organic synthesis," Coll Vol. III, Wiley, New York, N.Y., 1955, p. 112.
8. a) M.S. Kharasch and H.C. Brown, J. Amer. Chem. Soc., 64, 329 (1942).
   b) M.S. Kharaseh and H.C. Brown, J. Amer. Chem. Soc., 62, 454 (1940).
9. E. Hedaya and L.M. Kyle, J. Org. Chem., 32, 197 (1967).
10. I. Tabushi, J. Hamuro, and R. Oda, J. Org. Chem., 33, 2108 (1968).
11. T. Tominaga, Y. Odaira, and S. Tsutsumi, Bull. Chem. Soc. Japan, 37, 596 (1964).
12. Y. Shigemitsu, T. Tominaga, T.S. Himodaira, Y. Odaira, and S. Tsutsumi, Bull. Chem. Soc. Japan, 39, 2463 (1966).

13. W. Reusch and C.L. Karl, Abstract of the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p. 79.

14. W. Reusch, C.K. Johnson, and J.A. Manner, J. Amer. Chem. Soc., 88, 2803 (1966).

15. H. Reimann, A.S. Caponaggi, T. Strauss, E.P. Oliveto, and D.H.R. Barton, J. Amer. Chem. Soc., 83, 4481 (1961).

16. M.F. Flies, R. Lalonde, and B. Maillard, Tetrahedron Lett. 6, 439 (1976).

17. L.W. Menapace and H.G. Kuivila, J. Am. Chem. Soc., 86, 3047 (1964).

18. a) D.D. Tanner and F.C.P. Law, J. Am. Chem. Soc., 91, 7535 (1969).

    b) A.L.J. Beckwith and C.B. Thomas, J. Chem. Soc., Perkin Trans. 2, 821 (1973).

    c) G. Brunton, K.U. Ingold, A.L.J. Beckwith, and P.J. Krusic, J. Am. Chem. Soc., 99, 3177 (1977).

19. C.M. Rynard, C. Thankachan, and T.T. Tidwell, J. Amer. Chem. Soc., 101, 1196 (1979).

20. K. Heusler and J. Kalvoda, Angew. Chem., Int. Ed. Engl., 3, 525 (1964).

21. L. Kaplan, J. Amer. Chem. Soc., 88, 1833 (1966).

22. W.H. Urry, A. Nishihara, and J.H. Niu, J. Org. Chem., 32, 347 (1967).

23. C. Walling "Free Radicals in Solution", John Wiley and Sons, Inc., New York, N.Y., 1957, pp. 277, 286.

24. C. Walling and A. Padwa, J. Amer. Chem. Soc., 85, 1593 (1963).

25 E.L. Cochran, F.J. Adrian, and V.A. Bowers, J. Chem. Phys., 86, 1938 (1862).

26. R.A. Kaba, D. Griller, and K.U. Ingold, J. Amer. Chem. Soc., 96, 6202 (1974).

27. D. Griller and K.U. Ingold, J. Amer. Chem. Soc., 96, 6203 (1974).

28. D. Griller, P. Schmid, and K.U. Ingold, Can. J. Chem., 57, 831 (1979)

29. D.G. Hawthrone and D.H. Solomon, J. Macromol. Sci. Chem., 9, 149 (1975).

30. J. Kalvoda, Helv. Chim. Acta, 51, 267 (1968).

31. D.S. Watt, J. Amer. Chem. Soc., 98, 271 (1976).

32. R.W. Freerksen, W.E. Pabst, M.L. Raggio, S.A. Sherman, R.R. Wroble, and D.S. Watt, J. Amer. Chem. Soc., 99, 1536 (1976).

33. M.L. Poutsma and P.A. Ibarbia, J. Org. Chem., 34, 2848 (1969).

34. R.W. Begland and D.R. Hartter, J. Org. Chem., 37, 4136 (1972).

35. W. Kemula and K. Wierzchowski, Koczniki Chem., 27, 527 (1953); Chem. Abstr., 48, 6253 (1954).

36. W.J. Linn, Unpublished obersvation, F.C. Schaefer, in "The Chemistry of Cyano Group," Ed. Z. Rappoport, Wiley, New York, N.Y., 1970, p. 581.

37. M.E. Childs and W.P. Weber, J. Org. Chem., 41, 3486 (1976).

38. O.W. Webster, D.R. Hartter, R.W. Begland, W.A. Sheppard, and A. Cairnscross, J. Org. Chem., 37, 4133 (1972).

39. W.J. Linn, O.W. Webster, and R.E. Benson, J. Amer. Chem. Soc., 87, 3651 (1965).

40. For complete procedure of analysis of noncondensable and condensable gases see Chapter 2.

41. F.C. Schaefer in "The Chemistry of Cyanogroup", Z. Rapport, Ed. Wiley, New York, N.Y., 1970, p. 289.

42. L.L. Bircumshaw, F.M. Tayler, and D.H. Whiffen, J. Chem. Soc., 931 (1954).

INTRODUCTION

PART II

The sensitivity of radical reactions to polar substituents was recognized in numerous publications between 1945-1948.[1-5] The authors explained the observed effects as arising from the contribution of dipolar structures to the stabilities of the transition states. In subsequent years, polar effects have been used to rationalize the selectivity of carbon hydrogen bond rupture by numerous radicals.[6-9] Walling and Mayo were the first to apply the Hammett equation to radical reactions.[5] Russell subsequently demonstrated that a number of pieces of data taken from the literature gave excellent correlation with σ^+ substituent constant.[10] Recently Blackburn and Tanner[11] reported the correlation of the relative reactivities, toward reduction by tri-*n*-butylstannane, of a series of substituted benzyl halides with σ^- substituent constant.

The transition state for hydrogen abstraction reactions is dependent upon the reactivity and the electron affinity of the attacking radical ($X^{\cdot}$), and either structure I, II or III may predominate.[10,12]

$$X^{\cdot} + RH \longrightarrow XH + R^{\cdot} \qquad (1)$$

$$[X^{-}\cdots H\cdots {}^{+}R \longleftrightarrow X\cdots H\cdots R \longleftrightarrow X^{+}\cdots H\cdots {}^{-}R]^{\ddagger\cdot} \qquad (2)$$

I II III

For radicals or atoms with a low electron affinity such as $CH_3^{\cdot}$, $C_6H_5^{\cdot}$, $H^{\cdot}$, $\underline{p}$-$CH_3C_6H_4^{\cdot}$, the transition state is predicted to be best described by connonical form II, where there is no charge separation, since there is little or no difference between the electronegativities of the attacking radical ($X^{\cdot}$) and the carbon center in RH. In the case of <u>para</u>- and <u>meta</u>-substituted toluenes this prediction has been substantiated since for the radicals $H^{\cdot}$,[13] $C_6H_5^{\cdot}$,[14] $\underline{p}$-$CH_3C_6H_4^{\cdot}$[15] and $CH_3^{\cdot}$[16] the rho values observed are very close to zero. However, for highly electron deficient atoms or radicals, for instance, $Cl^{\cdot}$, $CCl_3^{\cdot}$, $Br^{\cdot}$ the transition state can be approximated by connonical form I, where there is a large charge separation in the transition state. For these radicals and atoms a pronounced polar effect is expected. Consequently, substantially larger substituent effects were observed in hydrogen abstraction from <u>meta</u>- and <u>para</u>-substituted toluenes by $Cl^{\cdot}$;[17] $\rho = -0.7$ (Cl_2, CCl_4), $CCl_3^{\cdot}$;[18] $\rho = -0.69$, $Br^{\cdot}$;[19,20] $\rho = -1.4$ (Br_2, CCl_4). Finally the observation of correlation of relative reactivity with σ^{-} in reduction of benzyl halide by tri-<u>n</u>-butylstannane, by Blackburn

and Tanner,[11] infers that bond breaking takes place in the transition state and that the connonical form III is the dominant contributor to the transition state. The magnitude of rho reflects the reactivity of the attacking radical i.e., the contribution of connical forms I, II or III to the transition state. For instance the somewhat low value of rho, -0.7, for the chlorine atom indicates the low degree of bond breaking in the transition state. For the less reactive bromine atom which has an electron affinity similar to that of chlorine the rho value, -1.4, is indicative of more extensive bond breaking in the transition state. From these observations it was predicted that for a radical with a high degree of electron affinity, rho should increase with the extent of bond breaking.

These observations clearly demonstrate that an extremely useful technique for probing the contribution of these polar effects is the application of the Hammett $\rho\sigma$ equation. The Hammett equation has been applied to many types of free radical reactions including, atom transfer,[21-28] additions,[27,29] copolymerization,[21] initiator decompositions,[21,30] disproportionations[31] and β-scissions.[32]

The polar effect argument has also been used to rationalize the intramolecular selectivity data for a series of n-alkyl derivatives (see Table 1).

TABLE 1

Substitution in n-Propyl and n-Butyl Derivatives[a]

Reagents	R————	% Substitution CH_2—CH_2—CH_3			% Substitution on R
Cl_2, 68°, liquid	CH_3-	32	32	18	18
Cl_2, 34°, liquid	$ClCH_2$-	24	51	18	7
Cl_2, 16°, liquid	F_3C-	0	45	55	-
Cl_2, CCl_4	HO_2C-	8	52	40	-
Cl_2, 25°, liquid	CH_3O_2C-	13	61	24	-

a) Taken from ref. 26, p. 306.

The results from this table show that the ability of a substituent to direct the attack of a radical with a high electron affinity to a remote part of the molecule increases in the order of, $-CF_3 > -CO_2H > CH_3COO- > -CH_2Cl > CH_3$. A positive-charged radical or substrate magnifies this effect as evidenced by a comparision of the values for $Cl^{\cdot}$ and $((CH_3)_2CH)_2NH^{+\cdot}$ in the chlorination of hexanoic acid (see Table 2).

TABLE 2

Chlorination of Hexanoic Acid, % Substitution at 25°[a]

Reagents	HO_2C-CH_2-CH_2-CH_2			CH_2-CH_3	
Cl_2, CCl_4	4	13	28	37	18
Cl_2, 90% H_2SO_4	4	7	40	7	42
$((CH_3)_2CH)_2NH^+Cl$, $h\nu$, H_2SO_4	0	0	0	93	1

a) Taken from ref. 26, p. 308.

Protonation of the substrate and attack by a radical cation ($R_2NH^{+\cdot}$) show an extremely strong polar effect in that the site of attack is at the methylene group which is the furthest removed from the site of protonation. The preferred α attack by methyl radicals in propionic acid is sharply contrasted by the preferred β attack of chlorine atoms (see Table 3).

TABLE 3

Attack of Chlorine Atoms and Methyl Radicals upon Propionic Acid[a]

Radical	Relative reactivity per hydrogen atom		
	X——CH_2——CH_3		
$CH_3^{\cdot}$, 100°	HO_2C	7.8	1.0
$Cl^{\cdot}$, 80°	HO_2C	0.03	1.0

a) Taken from ref. 26, p. 311.

Since the bond dissociation energies are the same, [$D(CH_3\text{-}H)$ = 103 kcal/mol and D(H-Cl) = 103 kcal/mol][33] then the difference in product distribution must be due to polar effects.

The early treatment of the Hammett $\rho\sigma$ equation for polar effects by Walling[5] and Russell,[10] which has gained wide acceptance, has explicitly dealt with polar effects on transition states. The substituent effects on bond dissociation energies, which were thought to be small,[1,3] were ignored. In 1972, Zavitsas and Pinto[34] challenged the polar effects arguments. Zavitsas had previously shown that for hydrogen abstractions of the type $X\text{-}H + Y^{\cdot} \longrightarrow X^{\cdot} + H\text{-}Y$, accurate energies of activation could be obtained from a simple calculation.[35] The data needed are ir stretching frequency, BDE, masses, and bond length in the stable molecules X-H, H-Y, and X-Y. Anti-bonding interactions in X···Y in the transition state were found to be a major factor in controlling the energies of activation. The polarity of the X-Y bond is reflected strongly in the ir stretching frequency, which in turn affects the calculated antibonding energy. Thus, based on his semi theoretical calculations,[35] Zavitsas concluded that the qualitative concept of polar effect can be treated quantitatively without postulating charge separation in the transition state.

To support this argument, Zavitsas and Pinto[34]

presented a linear correlation between ρ and ΔH for the abstraction of hydrogen atoms from the ring substituted toluenes by $Cl^{\cdot}$, $Br^{\cdot}$, t-$BuO^{\cdot}$, $\dot{C}Cl_3$ and $C_6H_5^{\cdot}$. These workers suggested that the effects of polar substituents on transition-state stabilities were unnecessary considerations in rationalizing the relative rates of hydrogen transfer reactions of free radicals with substituted toluenes.

$$X^{\cdot} + ArCH_2\text{-}H \longrightarrow X\text{-}H + ArCH_2^{\cdot} \qquad (3)$$

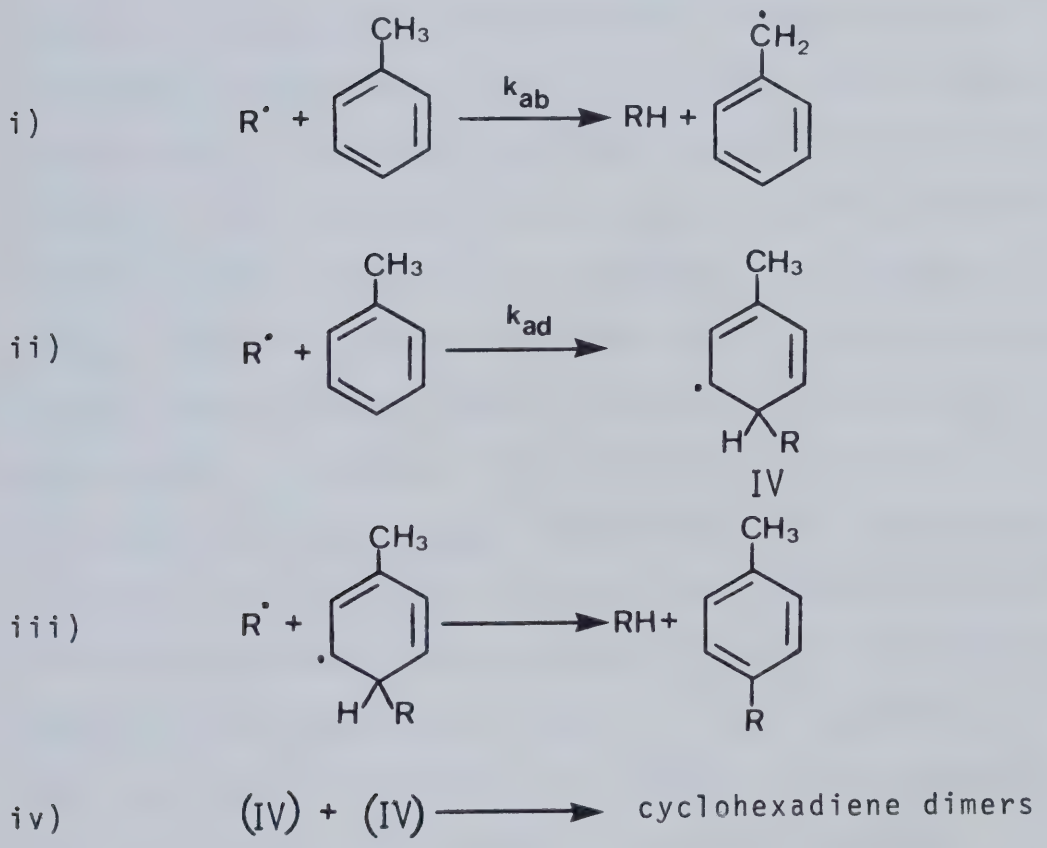
They proposed instead that the effects observed could be adequately explained on the basis of the changes effected by the substituents on the bond dissociation energy (BDE) of the benzylic C-H bond. Since only negative rho values had been reported for reactions analogous to equation 3, Zavitsas suggested that electron-donating substituents weaken benzylic C-H bonds and electron-withdrawing substituents strengthen these bonds, and that all such reactions must have negative rho values purely because of substituent effects on bond dissociation energies. Zavitsas, therefore, concluded that it would be impossible to obtain positive rho values for hydrogen abstraction reactions from toluenes.

There are, however, conflicting reports regarding the proposed linear relationship between ρ and ΔH. The

rho value for hydrogen abstraction from substituted toluenes had been determined for the tert-butyl peroxy radical, ρ^+ (t-BuOO·) = -0.56.[36] From the estimated BDE of t-BuOO-H,[37] it was pointed out by Howard, that the point for tert-butyl peroxy radical would not fit the $\rho/\Delta H$ plot. Tanner et al.[18], in a reinvestigation of the relative rates of the photoinitiated bromination of substituted toluenes with bromotrichloromethane, re-evaluated the rho value for trichloromethyl radical, ρ ($\dot{C}Cl_3$) = -0.69, and in that paper it was pointed out that this new point, which was one of the original points on the Zavitsas $\rho/\Delta H$ plot,[34] did not fit the plot.

At the time that the analyses of the substituent effects were published by Zavitsas,[34] only electrophilic radicals had been investigated. The negative rho values obtained in these studies could be rationalized, either by Zavitsas' proposal or by the traditional polar effect arguments. However, a number of studies involving the abstraction reactions of nucleophilic alkyl radicals from substituted toluenes were reported subsequent to Zavitsas' proposal. The alkyl radicals tert-butyl[38,39] (ρ = +1.0), isopropyl[39] (ρ = +0.8), undecyl[40,41] (ρ = +0.5), and 1-ethylpentyl[42] (ρ = +0.7) all were reported to show positive rho values. These observations contradict Zavitsas' argument that only negative rho values should be observed for hydrogen abstraction from toluenes.[34]

The validity of the published positive rho values has been questioned by Zavitsas.[43,44] According to the author, reported positive rho values for benzyl hydrogen abstraction from toluenes by undecyl,[40,41] 3-heptyl,[42] and tert-butyl[38] radicals, are the results of homolytic aromatic substitution (Scheme 1).



(SCHEME 1)

In the study of polar effects using the above radicals, the authors assumed that only the first of the four reactions shown in Scheme 1 is important. However, according to Zavitsas, cyclohexadienyl radical (IV) resulting from additon of the radical ($R^{\cdot}$) to the aromatic ring, is potentially a hydrogen donor (see Scheme 1). A qualitative estimate of ring addition compared to benzylic hydrogen abstraction was made by determining the relative reactivities of substituted toluenes and the analogously substituted benzenes toward undecyl radicals. From an analysis of this data he concluded that considerable ring addition had occurred with both aromatic systems which contain electron-withdrawing substituents, whereas benzylic hydrogen abstraction was the predominant process with toluene substrate having electron-donating substituents. A Hammett plot of total reactivity (ring addition and hydrogen abstraction) of the toluenes was shown to give a rho value of +0.4. From the small positive rho value, Zavitsas concluded that the positive Hammett slopes reported by Pryor[38,39] and Henderson[42] were the result, primarily, of addition to the aromatic ring, rather than abstraction of benzylic hydrogen.

In contrast to the report by Zavitsas[43,44] that the observed positive rho for alkyl radicals is because of the importance of radical addition to the ring, Pryor[40] found a negligible amount of undecyltoluene and

no cyclohexadienyl dimers in the reaction of undecyl radicals with toluenes. Tanner[45] also reported insignificant amount of addition of 1-ethylpentyl radicals to toluene (~0.4%) and estimated, k_{ab}/k_{ad} to be between 6×10^{-3} and 8×10^{-3}.

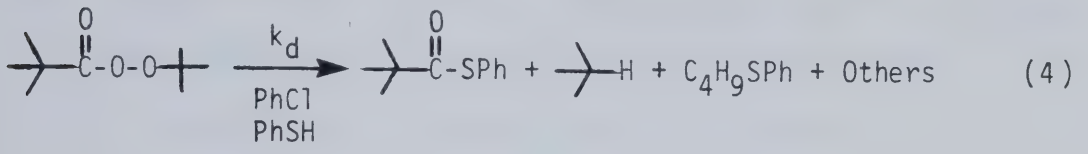
More recently Tanner et al.[46] questioned the experimental validity of the positive rho values in the reaction of alkyl radicals with substituted toluenes and pointed out that the reactivity of a relatively unselective carbon-centered alkyl radicals, not attached to a highly electronegative atom, would show little or no correlation to substituents and would be predicted to have a relatively small value of rho. In agreement with this prediction the rho value found by Russell for phenyl radical abstraction[14] was -0.1, and that found by Pryor for methyl[16] was -0.2 ± 0.2. It was pointed out by Tanner[46] that in the light of these predictions, the high positive rho values reported for hydrocarbon radicals (undecyl, +0.5; isopropyl, +0.8; 1-ethylpentyl, +0.7; tert-butyl, +1.0) were surprising since their reactions should be quite exothermic and unselective ($-\Delta H \simeq$ 6-13 kcal/mol) and their difference in electronegativity compared to the benzyl carbon should be rather small.

In reexamining the experimental data which lead to the proposal of the positive rho value for 1-ethyl-

pentyl radicals,[42] Tanner et al.,[45] showed that the relative rates of hydrogen abstraction from toluenes and chlorine from carbon tetrachloride, k_H/k_{Cl}, change only by a factor of ~3 when the substrate was changed from toluene to p-cyanotoluene. Furthermore under the most favorable conditions for the formation of hydrocarbon, the yield of heptane amounts to only 0.5-0.75% of the 1-ethylpentyl radicals produced. Since the radical disproportionation products, 2-heptene, 3-heptene and trans-stilbene were produced in much higher yield than the heptane itself, it was not experimentally possible to determine the genesis of this small amount of heptane that may have been formed by abstraction from the toluenes or from disproportionation. It was evident from comparison of the yield of 3-chloroheptane (70%) to that of the hydrocarbon, that toluenes cannot compete effectively with carbon tetrachloride for 1-ethylheptyl radicals. On the basis of these experimental observations, the validity of the reported positive rho value for the 1-ethylpentyl radical was in question.[45]

In the course of the study of the decomposition of tert-butyl peroxypivalate (BPP) and its substituted homologues, Tanner et al.[47,48] had an interest in investigating the fate of tert-butyl radicals in aromatic solvents, in the presence of radical scavengers. They had noted that in the presence of thiophenol the uni-

molecular rate of decomposition of BPP was not constant, and that thioester (see equation 4) was the major product in the reaction.



(4)

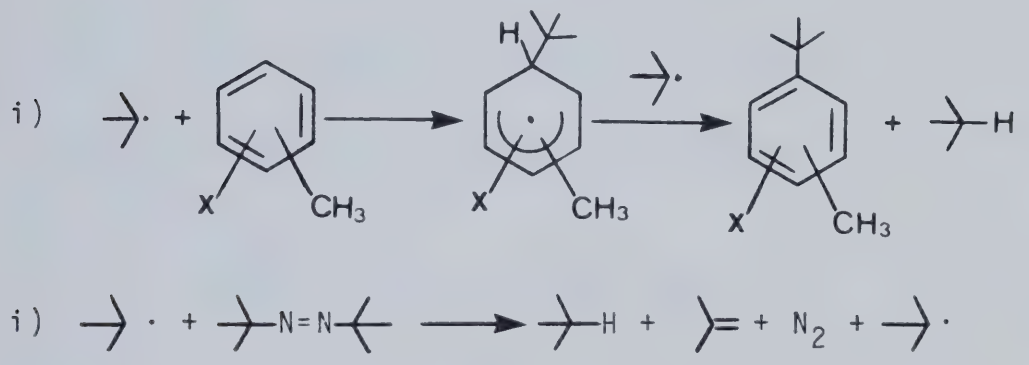
The positive rho value reported by Pryor for tert-butyl radical was based on studies of both BPP and 2,2'-azoisobutane (AIB) decompositions. Since there was a question concerning the mechanism of the BPP decomposition, the accuracy of the entire report was questionable. Furthermore the observed positive rho value of +1.0 for the tert-butyl radical, based on the previous arguments, seemed unreasonably high. Since no analysis of the products of decomposition was given, the reaction was reinvestigated.[46]

The method used by Pryor,[39] to obtain the relative selectivities for abstraction of the benzylic hydrogen by tert-butyl radicals, was a competitive one. Mixtures of a chosen, substituted toluene, and deuteriothiophenol, or tert-butyl mercaptan-d, were used as solvent in which to carry out the photochemical decomposition of 2,2'-azoisobutane (AIB) or BPP.

The tert-butyl radicals produced in the photolysis were presumed to competitively abstract either deuterium

from thiol (k_{SD}) or a protium from the benzylic position of the toluene (k_a). The ratio of isobutane to isobutane-2-d formed in the reaction (mass spectral analysis) was related to the relative rates of abstraction (k_a/k_{SD}).

The formation of isobutane conceivably arises from a number of alternative sources: (Scheme 2).



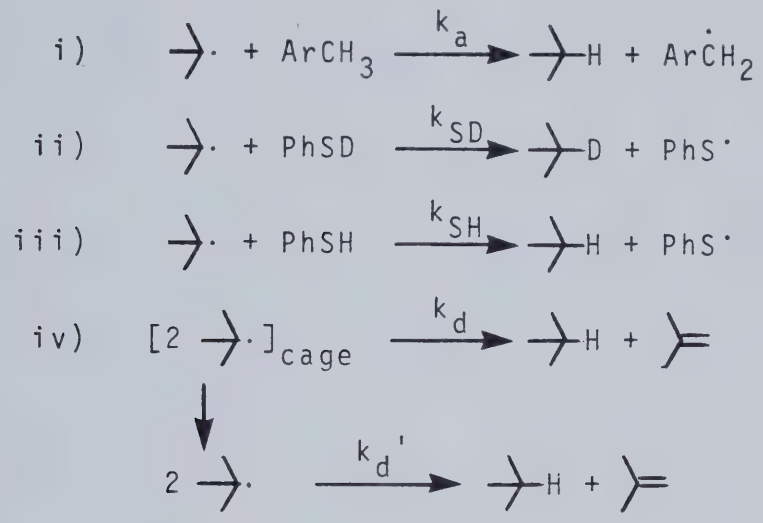
(SCHEME 2)

Addition of the tert-butyl radical to the aromatic ring to give a cyclohexadienyl radical [eq. (i) Scheme 2], followed by hydrogen abstraction by a tert-butyl radical could give isobutane. The importance of this pathway was ruled out by Pryor since no tert-butyltoluene could be detected in a reaction mixture obtained from the reaction of AIB in toluene containing thiophenol.

The induced decomposition of AIB [eq. (ii), Scheme 2] was also ruled out based on the result of the following experiments. Neither 2-cyano-2-propyl nor tert-butyl radicals, produced by thermolysis of azoisobutyronitrile or tert-butyl peroxypivalate at 80° in a solution of AIB in

toluene, caused the concentration of AIB to decrease.

The other sources of hydrogen which were considered in the formation of isobutane, are shown in Scheme 3.



(SCHEME 3)

Pryor[39] made the usual steady state assumptions, and derived the following kinetic expression using the reactions considered in Scheme 3.

$$\frac{d[\rightarrow H]/dt}{d[\rightarrow D]/dt} = \frac{k_a[ArCH_3]}{k_{SD}[PhSD]} + \frac{k_{SH}[PhSH]}{k_{SD}[PhSD]} + \frac{k_{dec}f_c[initiator]}{k_{SD}[\rightarrow\cdot][PhSD]} + \frac{k_d'[\rightarrow\cdot]}{k_{SD}[PhSD]} \qquad (5)$$

Where f_c is the fraction of the radicals which react in the cage and k_{dec} is the rate of decomposition of initiator. The equation (5) could not be integrated in this form. However, the authors made the following simplyfying

assumptions which allowed them to integrate the simplified equations:

It was recognized that isobutane may also be formed by disproportionation of the radicals produced from the decomposition of AIB both in the solvent cage and after escape from the cage (equation iv). The latter process was ruled out in the case of AIB by the demonstration that the absolute yield of combination product (2,2,3,3-tetramethylbutane), formed did not change with increasing thiol concentration. The low yield of dimer was used to estimate the extent of cage disproportionation. The ratio of ~5 for disproportionation to combination for tert-butyl radicals had previously been reported.[49] Since only a small amount of combination product was found, a limit of (~5%) was set on the importance of cage disproportionation. In the case of BPP isobutane does not form by cage disproportionation,[50] and it was assumed that, as in the case of AIB decomposition, the high concentration of scavengers (toluene and thiophenol) would scavenge any radicals which escape from the cage prior to self reaction.

The assumption that the last two terms in equation 5 (disproportionation terms) are negligible allowed them to integrate the expression and use the following integrated form, equation 6.

$$\frac{[\text{C}_6\text{H}_5\text{CH}_2\text{H}]}{[\text{C}_6\text{H}_5\text{CH}_2\text{D}]} = \frac{k_a[\text{ArCH}_3]}{k_{SD}[\text{PhSD}]} + \frac{k_{SH}[\text{PhSH}]}{k_{SD}[\text{PhSD}]} \qquad (6)$$

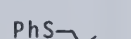
The complication due to the formation of isobutane from thiophenol impurity present in thiophenol-d [eq. (ii) Scheme 3] seemed to be unimportant since this ratio of H to D abstraction was constant in all of the relative reaction rates run. Since the last term in equation 6 is considered to be constant, k_a/k_{SD} for each toluene could be obtained from the slope of a plot of $[\text{C}_6\text{H}_5\text{CH}_2\text{H}]/[\text{C}_6\text{H}_5\text{CH}_2\text{D}]$ vs. $[\text{ArCH}_3]/[\text{PhSD}]$. If one assumed that k_{SD} was constant for a series of reactions carried out using different substituted toluenes then the relative rates of abstraction from these toluenes have been determined as the ratio of any two individual reactions.

The major limitation in using this kinetic analysis is the assumption that the benzylic hydrogen of the arylalkane was the only kinetically important source of protium available for the formation of isobutane.

However, the results obtained by Tanner et al.[46] on the photodecomposition of AIB and BPP in mixtures of thiophenol-d and toluenes are not in accord with those reached by Pryor.[38,39] The results of AIB photodecomposition are shown in Table 4.

TABLE 4

Photodecomposition of AIB (0.1 M) in Presence of PhSD(0.6-3 M)

Substrate $ArCH_3$						Uncorrected[a] Maximum Abstraction from $ArCH_3$ %	Corrected[b] Maximum Abstraction from $ArCH_3$ %
$C_6H_5CH_3$	73.5	48.0	13.7	9.80	31.4	28.4	8.2
$C_6H_5CH_3$	66.8	54.3	18.3	9.13	28.4	20.1	0.0(-2.7)
p-$ClC_6H_4CH_3$	72.2	46.4	29.4	7.7	28.9	13.9	2.8
p-$ClC_6H_4CH_3$	71.1	52.6	25.4	8.7	32.4	13.3	0.68
p-$CNC_6H_4CH_3$	82.7	36.0	37.5	10.9	21.6	23.6	16.0
p-$CNC_6H_4CH_3$	74.7	40.6	52.0	9.4	11.4	11.3	1.6
m-$ClC_6H_4CH_3$	73.1	44.4	42.7	10.5	14.0	16.4	0.0(-2.2)
p-$MeC_6H_4CH_3$	76.0	48.6	37.0	8.7	14.9	24.1	3.7
p-$MeC_6H_4CH_3$	69.7	55.8	37.5	9.1	18.3	13.9	0.51
m-$MeC_6H_4CH_3$	77.8	46.1	21.8	10.4	26.8	29.2	9.8
p-$C_6H_5OC_6H_4CH_3$	84.7	27.1	36.4	8.1	35.2	13.1	7.4
p-$C_6H_5OC_6H_4CH_3$	87.3	26.9	40.2	7.6	31.8	15.3	9.6
m-$C_6H_5OC_6H_4CH_3$	82.0	26.0	61.4	8.1	12.4	8.2	2.7
m-$C_6H_5OC_6H_4CH_3$	78.7	26.7	52.1	8.9	21.1	5.5	0.0(-0)

a) Calculated as $([C_4H_{10}] - [C_4H_8] - [C_4H_8DSC_6H_5])$.

b) Calculated as $[C_4H_{10}]_{total} - [C_4H_9D]f$, where f is the ratio $f = \{[C_4H_{10}]_{total} - ([C_4H_8] + [C_4H_8DSC_6H_5])\}/[C_4H_9D]$, found in the decomposition of AIB in mixtures of Freon and thiophenol-d.

The relative reactivities for the decomposition reactions of toluene solutions of AIB (0.1 M) in thiophenol-d (0.6 and 3 M) were calculated from the data collected in Table 4 according to the method previously reported.[42] Hammett plots of log k_a/k_a^o vs. the substituent constants, σ, gave positive rho values, in agreement with Pryor and Davis,[38,39] although their magnitudes (+0.53 and +0.55) are not so large as that previously reported, +1.0. This discrepancy was attributable, however, to the difference in the method used to calculate the product ratios obtained from the data collected from the mass spectral analysis.[46]

From the examination of Table 4, it is obvious only (0-16%) of isobutane is formed by benzylic hydrogen abstraction. A large portion of the tert-butyl radicals (~25%) abstract deuterium from thiophenol-d. The major fraction of the remaining tert-butyl radicals appears to disproportionate to form isobutylene plus its disproportionation partner isobutane. The isobutylene plus its addition product and an equivalent amount of isobutane formed by disproportionation account for 71-95% of the tert-butyl radicals that do not form deuterated isobutane. The disproportionation reaction was shown to be a cage process, since the absolute amount of isobutylene did not change by varying the concentration of the scavenger, thiophenol-d.

Since it has now been shown that the third term (cage disproportionation) in equation 5 was a major term, the expression does not appear to be easily integratable and equation 6 is no longer valid.

However, the systematic variation of k_a/k_{SD}, which was obtained by determining the ratio of products $[C_4H_{10}]/[C_4H_9D]$, could be related to the viscosity of the substrates (solvents).[46] A plot of the logarithm of the viscosity of each substrate relative to toluene vs. the substituent constant, σ, gave a good correlation when the values for m- and p-phenoxytoluene, were excluded.

Noyes' model (equation 7) for the solvent cage reactions predicts that the fraction of bimolecular reactions, F = (1/cage efficiency)-1, which take place in the solvent cage should correlate with the fluidity of the solvent, $1/\eta$.[51]

$$F = \left(\frac{R_o - 2b}{2b}\right) + \left(\frac{R_o}{2b}\right)\left[\left(\frac{A_T + \alpha A_E}{\alpha}\right)\left(\frac{1}{\eta}\right) + \left(\frac{A_T \cdot A_E}{\alpha}\right)\left(\frac{1}{\eta}\right)^2\right] \qquad (7)^*$$

Since, m- and p-phenoxytoluene are both solvents of high viscosity it was not surprising that they did not

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* In this equation R_o, is the initial separation of the fragments due to intervening molecules, A_E, the translational energy of the separating fragments, A_E, A_T, the mass and radius of the fragments, and α, the probability per collision that the pair will react.

fit the plot of log (relative viscosities) vs. σ. A plot of log (relative rates) vs. fluidity of the solvents however, did give an excellent correlation.

Since k_a/k_{SD} appeared to be related to the viscosity of the media, the relationship suggested by equation 7 should be applicable in the present system. The Noyes' model was tested by plotting 1/cage yield vs. the fluidity of the solvent. An excellent correlation was obtained which clearly demonstrated that the cage yield of isobutane, the major fraction of isobutane formed, was directly controlled by the viscosity of the solvent. Since it is believed that the cage decomposition products of BPP do not yield isobutane,[50] the observation by Pryor and Davis[38,39] that the relative rates derived from the perester decomposition also correlate with σ is an anamoly and, therefore, must be due to effects other than the solvent viscosity. A plot of σ vs. log (k_a/k_a^{o}) obtained from the data collected in the study reported by Tanner et al.,[46] for the BPP decomposition did not give a satisfactory correlation. The discrepancy between the study by Pryor[39] and Tanner[46] on the decomposition of BPP may have been due to the more rigorous mass spectral analysis, in the latter work, of the hydrocarbons produced in the reaction.

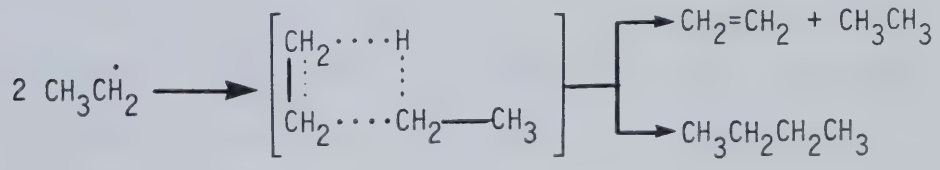
It was concluded from this work that the positive ρ value reported for tert-butyl[38,39] radicals either showed no correlation (BPP decompositions) or was an artifact of

an experimentally observed cage disproportionation reaction (AIB decompositions).

Careful examination of Table (4) reveals that the disproportionation to combination ratio, k_d/k_c, is not constant over the range of solvent viscosities used (0.56-3.46 cP). However, at that time the variation, (k_d/k_c = 4.6-9.2) was attributed to the experimental difficulties encountered in the analysis of the small amounts of combination product, 2,2,3,3-tetramethylbutane, produced. The hydrocarbon is highly volatile, and more than usual care is required for its analysis (the absolute amount of combination product was found by Tanner[46] to be ten times larger than that reported by Pryor).[38,39]

The factors which are known to influence the ratio of disproportionation vs. combination must now be discussed.

In the early studies of radical-radical termination processes, a common four centered transition state was proposed for the termination reaction of two ethyl radicals:[52,53]



(8)

This proposal was based on the very small dependence of k_d/k_c on temperature ($k_d/k_c \propto T^{-0.7}$)[52] or k_d/k_c = 0.087 exp (371/RT).[54] However Gillis[55] found a temperature dependence for k_d/k_c = 5 exp (290/RT) for ethyl radicals

in liquid methane, and suggested that combination and disproportionation might proceed by way of different transition state. Gillis argues that these findings are compatible with the proposal made by Benson[56] that both reactions involve transition states with considerable ionic character, but that the transition states are different, and that there could be more contribution from ionic states to the transition state for disproportionation than for combination. Solvation in the liquid phase, even in a nonpolar liquid like methane, would therefore be expected to favor disproportionation. The lack of a significant temperature dependence of the k_d/k_c ratio observed for alkyl radicals has also been rationalized in terms of difference in entropy for the two processes:[57]

$$\log (k_d/k_c) = a (\Delta S_d^{o} - \Delta S_c^{o}) + b \qquad (9)$$

where $a = \beta/2.3\ R$ and $b = \beta (\Delta H_c^{o} - \Delta H_d^{o})/2.3\ RT$ + constant. The above equation is representative of a straight line only if b is constant. However, Konar[58] and Laidler[59] using data available in the literature failed to find a correlation between k_d/k_c ratios and ΔS values via equation 9.

Another factor which could influence the k_d/k_c ratio ratio is a steric effect. Rüchardt,[60] using data taken from the literature, showed that the ratio of disproportionation-combination of a number of alkyl radicals

correlate with the Hancock[61] steric parameter, E_s^c. The alkyl radicals used in this study are shown below:

$C_2H_5^{\cdot}$, n-$C_3H_7^{\cdot}$, i-$C_3H_7^{\cdot}$, s-$C_4H_9^{\cdot}$; t-$C_4H_9^{\cdot}$, $Et_3C^{\cdot}$.

The radicals are arranged in the order of increasing E_s^c values and k_d/k_c ratios.

This relationship however breaks down when applied to radicals which can be stabilized by resonance. For instance, the point for the cumyl radical (E_s^c = 2.35,[62] k_d/k_c = 0.06) did not fit the original plot of k_d/k_c ($n_{\beta H}$) versus E_s^c.

It has been shown[64] that the disproportionation-combination ratio is specific for each radical and further that the extent of disproportionation of simple alkyl radicals increases with an increase in the number of β-hydrogens available for transfer (Table 5).

TABLE 5

Disproportionation-Combination Ratios (k_d/k_c) for Alkyl Radicals in Solutions at 30°[64]

Alkyl radical	Solvent	k_d/k_c	$k_d/k_c(n)$
$CH_3CH_2^{\cdot}$	Decalin	0.12	0.04
$CH_3CH_2CH_2^{\cdot}$	Decalin	0.13	0.075
$CH_3\dot{C}HCH_3$	Decalin	1.2	0.20
$CH_3-\dot{C}(CH_3)-CH_3$	n-pentane	7.2	0.80

The n is the last column is the number of available β-hydrogen atoms.

The normalized values of k_d/k_c in Table 5 clearly indicate that the factors affecting disproportionation are more than simple statistical ones. It has been suggested that orientation of the radicals may influence combination,[65,66] that is, for large radicals such as tert-butyl, rotation is slow relative to the duration of an encounter and only a small number of radicals are correctly oriented for combination during each encounter. On the other hand, disproportionation is much less favorable when the radical is stabilized by delocalization of the unpaired electron. For instance, k_d/k_c per β-hydrogen is 0.023 for 1-phenylethyl radical[67] and 0.06 for cumyl.[63]

The first report of the dependence of, k_d/k_c on media (solvent) was reported by Stefani[68,52] in the photolysis of azoethane in different solvents at 65°C (Table 6). A linear relationship was obtained between k_d/k_c and the square root of the internal pressures of the solvents employed. The values of k_d/k_c changed about 66% from the lowest value in isooctane, to the highest, in ethylene glycol. In the same study Stefani showed that the k_d/k_c ratio was temperature dependent. On the basis of these observations the authors[68,52] suggested that the k_d/k_c ratio is a function of the "internal pressure" of the solvent. Dependence of the k_d/k_c ratio on solvation of

TABLE 6

Disproportionation-Combination of Ethyl Radical as a Function of Solvent, 65°[68]

Solvent	Scavenger	k_d/k_c
Gas phase	None	0.14
Isooctane	None	0.144±0.003
Isooctane	Sytrene	0.145±0.007
Limonene	None	0.158±0.005
Ethylbenzene	None	0.156±0.001
m-Xylene	None	0.165±0.003
Toluene	None	0.167±0.003
2-Butanol	None	0.168±0.003
2-Propanol	Styrene	0.178±0.001
1-Propanol	Styrene	0.181±0.003
Aniline	Styrene	0.195±0.001
Acetonitrile	None	0.200±0.006
Acetonitrile	Styrene	0.208±0.006
Ethylene glycol	None	0.241±0.003

radicals was ruled out by Stafani on the basis of the observation that no correlation was found between the k_d/k_c ratio and the dielectric constant of the solvents. However Kochi,[64] in an investigation involving a variety of alkyl radicals, showed that the k_d/k_c ratio remained the same in hydrocarbon solvents, using pentane, decalin and Nujol, although the "internal pressure" varies widely in these solvents.

For radicals where no disproportionation is possible Szwarc[65,66] demonstrated that the probability of the cage combination of geminately formed trifluoromethyl radicals ($\cdot CF_3$) obtained from the photolysis of 1,1'-azobistrifluormethane, increases with decreasing temperature and increasing viscosity of the solvent (Table 7).

TABLE 7

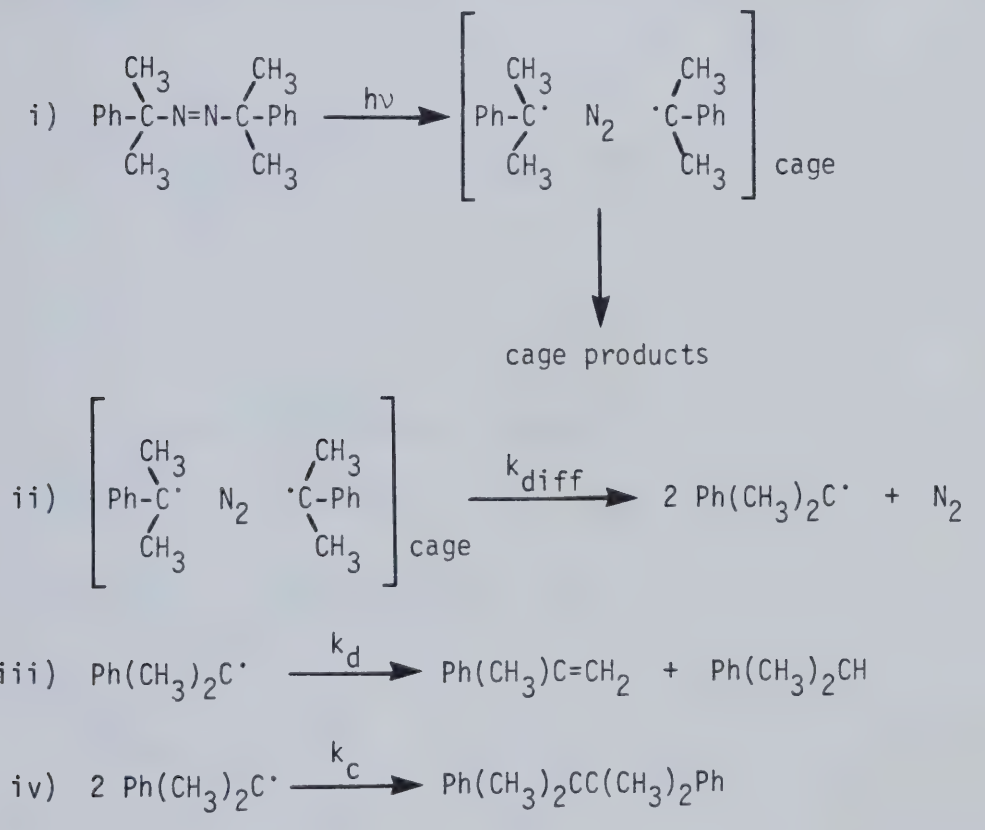
Probability of Cage Combinations of CF_3 Radicals in Solvents of Different Viscosities[75]

Solvent	η(cP,21°)	C_2F_6/N_2* 0°	30°	90°
2-Methylbutane	0.232	0.3	0.21	0.11
Isooctane	0.484	0.49	0.40	0.24
Carbon tetrachloride	0.944	0.64	0.51	0.34
Decalin	2.85	0.77	0.69	0.50

*Probability of cage combination was calculated as C_2F_6/N_2 ratios.

However, the probability of combination of caged methyl radicals was found to be much higher than that found for trifluoromethyl radicals. The authors suggested that this might be due to the higher rate of rotation of methyl when compared with trifluoromethyl.

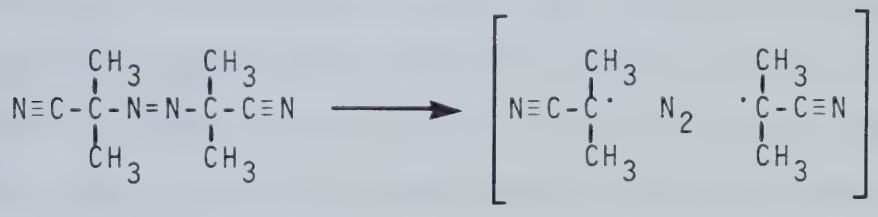
The variations in disproportionation and combination products were also reported by Nelsen and Bartlett[63] in the study of the photodecomposition of azocumene (Scheme 4).



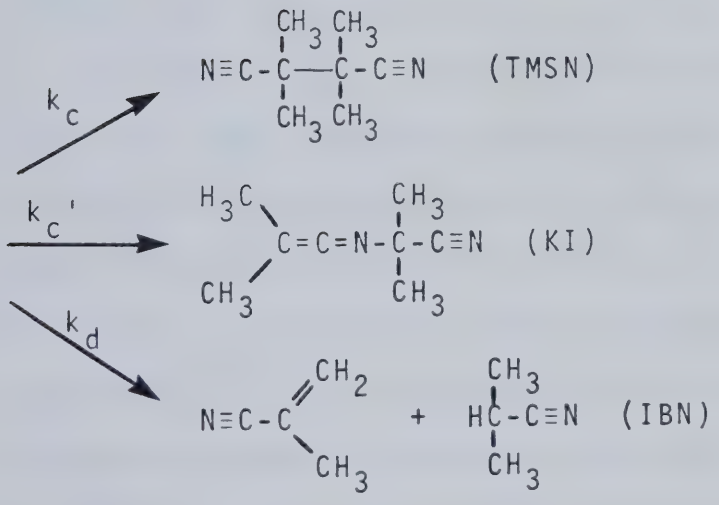
(SCHEME 4)

In benzene solution at 20.5°, cumyl radicals couple predominantly to give bicumyl with k_d/k_c =

0.06 and in frozen benzene, at about -8°, disproportionation and combination occur at almost the same rate, k_d/k_c = 0.93-1.05. However no convincing explanation was given for the difference of k_d/k_c in solution and solid benzene. The medium effects on disproportionation-combination ratios have also been studied by McBride[69,70] using the photodecomposition of azobisisobutyronitrile (AIBN), as a model reaction (Scheme 5).



AIBN



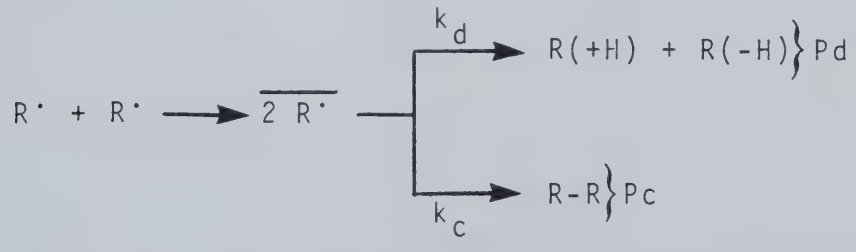
(SCHEME 5)

Photolysis of AIBN in benzene solution produced ~40% tetramethylsuccinonitrile (TMSN), ~5% isobutyronitrile (IBN) and ~55% ketenimine (KI). However, photolysis of crystalline solid AIBN produced ~96% IBN, ~4% TMSN and <0.5% KI. The amount of disproportionation product (IBN) is produced in an increased amount at the expense of the symmetrical combination product (TMSN), as the viscosity of the medium is increased. This observation was rationalized in the following manner: A disproportionation reaction, to yield IBN, requires only the movement of the nitrogen Molecule and the rotation of one methyl group; while a motion of the nitrogen and all of the atoms of at least one radical would be required to form the coupling product. The more viscous medium hinders the latter process.

Different k_d/k_c ratios have also been reported for tert-butyl and isopropyl radicals in different media. The ratio of disproportionation-combination for tert-butyl radicals changes from 2.3-4.5 in the gas phase[64] to ~7.2 in n-pentane to ~500 in the solid phase (isobutylene).[71,72] For isopropyl radicals, the k_d/k_c ratio has been reported to change from 0.65-1.1 in the gas phase[64] to 1.2 in decalin[64] to 1.6-2 in solid phase[71,72] (photolysis of azoisopropane at -195°).

Very recently Fischer[73] reported the viscosity dependence of the product distribution obtained from the

self reaction of tert-butyl radicals. The report appeared to have a significant bearing on the seemingly inconsistent k_d/k_c ratios observed by Tanner.[56] In a previous paper Fischer[84] had shown, from the study of the photolysis of di-tert-butylketone, that the self termination rate constant k_t, $(k_c + k_d)$ of tert-butyl radicals, R·, in solution is governed by translational diffusion, i.e. every encounter of two "free" radicals, that forms a caged singlet pair before reaction, results in formation of products; isobutane, R(+H); isobutylene, R(-H); and 2,2,3,3-tetramethylbutane, R-R.



(10)

The termination rate constant for two tert-butyl radicals was shown to be diffusion controlled,[74] $7 \times 10^7 < 2k_t < 2 \times 10^{10}$ $M^{-1}s^{-1}$, and increased not only by increasing temperature but also with decreasing solvent molecular weight (Table 8). Furthermore a linear relationship was found between the termination rate constant ($2k_t$), and the reciprocal of viscosity (T/η) of the media, i.e. for non-associating liquids.

TABLE 8

Termination Rate Constant of tert-Butyl Radicals[74]

Solvent	T [K]	k_t 10^9 $M^{-1}s^{-1}$
$n\text{-}C_8H_{18}$	297	2.7
	326	3.8
	343	4.9
	367	7.2
$n\text{-}C_{10}H_{22}$	297	2.4
	325	3.0
	343	4.6
	367	6.2
$n\text{-}C_{14}H_{30}$	297	1.4
	326	2.4
	344	3.3
	368	4.5

Similarly, the product ratios, P_d/P_c, produced from the reactions, were studied as a function of their variation as a result of running the decompositions in a variety of solvents and at different temperatures[73] (Table 9). From these results, Fischer concluded that the controlling factor which determined the variation in the product ratios was the viscosity of the media. A correlation of k_d/k_c with the entropy difference between disproportionation and combination products could be excluded based on the marked temperature dependence of k_d/k_c and strong medium effects for tert-butyl

TABLE 9

Disproportionation-Combination Ratios, k_d/k_c, for the Self-Reaction of tert-Butyl Radicals[73]

Solvent	T [°C]	k_d/k_c
$n\text{-}C_8H_{18}$	25	5.4
	50	4.4
	87	4.1
$n\text{-}C_{10}H_{22}$	25	5.7
	50	4.6
	87	4.3
$n\text{-}C_{12}H_{26}$	25	5.9
	50	4.9
	69	4.7
	87	4.5
$n\text{-}C_{14}H_{30}$	25	6.4
	50	5.1
	87	4.7
$n\text{-}C_{16}H_{34}$	25	6.9
	50	5.4
	69	5.0
	87	5.0
t-BuOH/Pinacol 1:2	8.5	23.5
	14	13.3
	25	10.1
	25	10.4
	49	8.3
	88.5	5.5

radicals in the liquid phase (Table 9).

Solvation effects were shown not to be in accord with the increase of k_d/k_c with the chain length of the n-alkane solvents. There is, however, a limited correlation in Fischer's data between internal pressure of the solvent and k_d/k_c ratio. Indeed, the trend of the internal pressure p_i in n-alkane solvents is similar to that of k_d/k_c, i.e., p_i increases with the solvent chain length.[75] However, there is a discontinuity in the proposed relation between k_d/k_c and p_i at the gas-liquid change of phase. Going from gas phase to liquid the internal pressure changes by a factor of $\sim 10^3$, while k_d/k_c for tert-butyl radical changes by a factor of two or less.[64] This is in marked contrast to the more than five fold change of k_d/k_c for tert-butyl radical in the liquid phase, observed by Fischer, for a similar change in internal pressure.

The dependence of the product distribution on the viscosity of the medium is one of the criterion which is often diagnostic of a cage effect. The concept of a solvent cage was first proposed by Frank and Rabinowitch,[76] and was extended and elaborated by Noyes.[77-79]

The importance of cage reactions has been amply

demonstrated in a number of reactions involving geminate radical pairs.[80]

According to the Noyes' model, 1/cage efficiency (F) should be linearly related to the fluidity ($1/\eta$) of the media except in the most fluid solvents, where the square term, $(1/\eta)^2$, becomes important[80] (see equation 7). This linear relationship between 1/cage vs. fluidity ($1/\eta$), has recently been observed by Tanner et al., in the photodecomposition of 2,2'-azoisobutane.[46] Martin[81] on the other hand, has correlated the cage yield of ethane in the photodecomposition of azomethane to the internal pressure of the media.

The purpose of this portion of the study was to establish whether isopropyl radicals generated by the photodecomposition of azoisopropane (AIP), could competitively abstract hydrogens from substituted toluenes in the presence of thiophenol-d. The reported positive rho value of +0.8,[39] appeared unreasonably large for hydrogen abstraction reactions of a carbon centered radical.

It was shown[46] that the kinetic results which led to the proposal of a positive rho (+1.0)[39] for the tert-butyl radical was a consequence of a cage reaction. Since the reported positive rho value for the isopropyl radical was based on similar kinetic results,

it was necessary to reexamine the kinetics results reported for this secondary radical.

It has been shown[46] that the tert-butyl radicals obtained in the photodecomposition of AIB could not competitively abstract from toluene in the presence of thiophenol-d, and that the cage disproportionation reaction was the major pathway in the formation of isobutane. If these observations are correct, the reactions of tert-butyl radicals in solvents (substrates) which do not have any abstractable hydrogens, such as benzenes, should produce the same product ratios as were obtained in the corresponding toluenes. It was decided to examine the fate of isopropyl and tert-butyl radicals in inert solvents (arenes), in the presence of thiol, and compare the results of these decompositions with those obtained in the photolysis of AIB and AIP in toluene with added thiol. It has been proposed that the observed positive rho values reported by Pryor are due to the aromatic ring addition.[43,44] The results of the above experiments will provide information as to the validity of this proposal.

It was shown[46] that cage disproportionation reactions of tert-butyl radicals correlated with solvent viscosity from 0.56 to 3.6 cP. It was decided to extend the range of viscosities studied and to examine the relationship between the cage yield and the solvent

viscosity for both the photodecomposition of AIB and AIP.

Finally, the experimental results reported by Tanner[46] suggested that k_d/k_c for photodecomposition of AIB was not constant in solvents (toluenes) having varying viscosities. Fischer[73] has now provided a model which predicts a relationship between k_d/k_c and solvent viscosity for the encounter of two tert-butyl radicals. The relationship for both tert-butyl radicals and isopropyl radicals, which are generated geminately, by the photodecomposition of AIB and AIP, is to be investigated. Our results for geminately formed tert-butyl radicals, provide an opportunity to compare the viscosity dependence of k_d/k_c with those obtained by Fischer[73] for encounter reactions of tert-butyl radicals.

RESULTS

Products of the Reactions of Azoisopropane (AIP) with PhSD. Material Balance.

Solutions of AIP (0.1 M) and thiophenol-d (0.5 M) in a chosen toluene were photolyzed (20 h, 30°) to approximatley 42% completion. Analyses of the products obtained from the photodecomposition are listed in Table 10. The organic products accounted from 95 to 100% of the theoretical quantity of isopropyl radicals produced. The products resulting from the reactions of isopropyl radicals were propane, propane-2-d, propene, 2,3-dimethylbutane, and phenyl propyl-2-d sulfide. The percentage of decomposition was based on the amount of azoisopropane used. The analysis of noncondensable gases showed, beside nitrogen a small amount, about 9% (base on the nitrogen collected) of another noncondensable gas. Subsequent mass spectral analysis showed that this gas was a mixture of hydrogen isotopes (see experimental). It was clear that under the above conditions, thiophenol-d was also being photolyzed to produce a small quantity of noncondensable gas.[82] Due to this complication, the percentage yield of the products were based on the amounts of AIP consumed and not on the nitrogen (i.e, noncondensable gas) evolution.

The isomerization of AIP to isopropyl hydrazone was

Table 10. Photodecomposition of Azoisopropane (0.1 M) in Substituted Toluenes (30°) Containing Thiophenol-d (0.5 M).

Entry	Substrate $ArCH_3$	Non-Condensable Gases[a] mmol x100	Initial >N=N< mmol x100	Final >N=N< mmol x100	>N(H)-N< mmol x100	Used >N=N< mmol x100	Products, [mmol/mmol >N=N< (used)] x100					$\frac{\Sigma >\bullet}{>N=N<}$ (Used) x100
							>H	>D	⩥	><	PhS(D)	
1	$C_6H_5CH_3$	7.32	18.7	11.8	0.048	6.85	53.2	54.3	29.6	26.0	1.28	95.2
2	$C_6H_5CH_3$	7.50	18.8	12.1	0.020	6.67	55.3	56.3	31.6	28.4	1.88	100
3	$m\text{-}CH_3C_6H_4CH_3$	7.01	18.8	12.5	0.034	6.26	54.4	54.3	31.3	27.0	3.34	98.6
4	$m\text{-}CH_3C_6H_4CH_3$	7.68	19.2	12.4	0.034	6.76	55.9	54.4	30.4	27.2	2.91	99.0
5	$p\text{-}CH_3C_6H_4CH_3$	7.33	18.9	12.1	0.034	6.76	57.6	51.8	30.9	28.5	2.25	99.7
6	$p\text{-}CH_3C_6H_4CH_3$	7.70	18.9	11.9	0.034	6.97	59.6	50.7	30.6	28.3	1.82	99.6
7	$m\text{-}ClC_6H_4CH_3$	6.78	18.7	12.5	0.186	6.01	53.2	53.3	30.6	27.6	3.70	98.0
8	$m\text{-}ClC_6H_4CH_3$	6.95	18.7	12.5	0.217	5.98	52.8	54.4	32.1	28.2	4.21	99.9
9	$p\text{-}ClC_6H_4CH_3$	6.65	18.4	12.3	0.202	5.90	53.7	53.1	31.2	26.6	3.03	97.1
10	$p\text{-}ClC_6H_4CH_3$	7.22	18.4	12.0	0.171	6.23	55.2	50.1	31.7	27.5	2.84	97.4
11	$p\text{-}CNC_6H_4CH_3$	7.46	18.7	10.9	0.875	6.90	59.3	44.7	34.6	26.8	2.10	96.6
12	$p\text{-}CNC_6H_4CH_3$	7.36	18.5	4.95	7.00	6.55	63.9	42.1	34.7	26.3	1.33	97.3
13	$p\text{-}CNC_6H_4CH_3$	7.34	18.6	11.3	0.740	6.56	58.6	49.1	35.0	27.6	0.25	99.0
14	$p\text{-}C_6H_5OC_6H_4CH_3$	6.63	18.8	12.7	0.176	5.92	63.4	33.0	41.9	29.6	0.29	98.9
15	$p\text{-}C_6H_5OC_6H_4CH_3$	6.77	18.8	12.6	0.351	5.84	65.2	35.8	42.0	29.4	0.28	101
16	$m\text{-}C_6H_5OC_6H_4CH_3$	7.91	18.6	11.4	0.178	7.02	60.2	39.8	41.7	30.1	0.32	101
17	$m\text{-}C_6H_5OC_6H_4CH_3$	7.85	18.9	11.4	0.178	7.30	58.2	38.1	41.4	28.9	0.34	98.0

a) Contain N_2, H_2, HD and D_2 (see experimental).

shown to be a significant side reaction in p-cyanotoluene where the reaction occurred to the extent of about 13% (Table 10). It was shown however, that azoisopropane did not isomerize significantly to the corresponding hydrazone in the majority of the solvents, and under the reaction conditions employed.

Similarly photodecompositions of AIP (0.1 M) in the presence of thiophenol (0.5 M) in a variety of solvents (benzenes and Nujol) were carried out to about 42% completion. Analyses of the products obtained from these decompositions are listed in Table 11. The organic products accounted for from 92 to 100% of the theoretical quantity of isopropyl radicals produced. The products resulting from the reactions of isopropyl radicals were propane, propene, 2,3-dimethylbutane and phenyl propyl sulfide. The percentage of decomposition was based on the amount of the AIP consumed (Table 11). The analysis of the noncondensable gases showed that beside nitrogen, another gas, hydrogen, was formed in approximately 14% yield (based on the nitrogen collected), (see Experimental). The isomerization of AIP to isopropyl hydrazone was shown not to be a significant side reaction in the solvents used except in benzonitrile where the reaction occurred to the extent of about 11%.

The results of the photodecomposition of AIP in

Table 11. Photodecomposition of Azoisopropane (0.1 M) in a Variety of Solvents (30°) Containing Thiophenol (0.5 M).

Entry	Solvent	non-Condensable gases[a] mmolx100	Initial >N=N< mmolx100	Final >N=N< mmolx100	>N-N< mmolx100	used >N=N< mmolx100	Products, [mmol/mmol >N=N< (used)]x100 >H			Phs	Σ>N=N<(used) x100	% cage	k_d/k_c
1	$C_6H_5CH_3$	8.72	18.5	10.7	0.027	7.77	107.4	31.4	27.05	0.71	96.8	59.2	1.18
2	$C_6H_5CH_3$	8.70	18.4	10.5	0.027	7.87	108.4	30.4	25.90	1.24	96.0	57.6	1.22
3	C_6H_6	9.07	20.5	12.4	0.017	8.08	116.2	29.2	28.00	2.35	101.8	59.6	1.13
4	C_6H_6	7.43	19.0	12.4	0.011	6.60	107.7	32.6	28.50	1.04	99.1	62.2	1.18
5	C_6H_5CN	9.02	18.5	9.54	0.80	8.16	105.4	35.7	26.12	1.04	97.2	62.9	1.41
6	C_6H_5CN	8.43	18.4	9.74	0.70	8.00	103.8	34.3	26.30	1.04	95.8	61.6	1.34
7	C_6H_5CN	7.30	18.5	11.4	0.74	6.40	104.1	30.4	26.16	4.77	95.8	61.3	1.34
8	$(C_6H_5)_2O$	8.07	20.5	12.7	0.30	7.50	98.8	38.4	26.71	0.73	95.7	65.8	1.46
9	$(C_6H_5)_2O$	8.60	20.5	12.5	0.43	7.57	98.7	40.7	29.0	0.5	98.8	70.1	1.42
10	Nujol (L/H),(1/1)	10.9	18.8	10.6	0.08	8.12	90.2	40.1	33.34	0.81	98.9	74.3	1.23
11	Nujol (L/H),(1/1)	9.36	19.0	11.0	0.05	7.95	95.6	38.1	30.34	0.30	92.3	68.7	1.26
12	Nujol (L/H),(1/2)	10.0	19.0	10.5	0.09	8.41	85.0	39.5	31.00	-	93.2	70.5	1.27
13	Nujol (L/H),(1/2)	10.4	19.1	10.7	0.11	8.30	89.6	41.7	34.16	0.55	100.0	76.4	1.23
14	Nujol(H)	13.2	18.4	7.25	0.09	11.0	84.6	39.8	29.85	0.12	92.1	69.8	1.33
15	Nujol(H)	9.55	18.7	11.0	0.10	7.60	89.5	41.2	31.07	-	96.4	72.2	1.32

a) Contain N_2, and H_2 (see experimental).

toluene in the presence of varying amounts of thiophenol-d (0.11-1.48 M) are listed in Table 12.

The decomposition of AIP in benzene and toluene without added thiophenol yielded, besides nitrogen, propane, propene, 2,3-dimethylbutane, and isopropylbenzene, a number of minor products (>7). The minor products were detected by GLC, however they were not identified. The products identified, accounted for 76% of the isopropyl radicals produced. In toluene four new products were detected (GLC); bibenzyl, isobutylbenzene and a 1:3 mixture of o- and p-isopropyltoluene. A large number of unidentified products (>11, 6%) were also detected. The products identified in toluene accounted for 80% of the isopropyl radicals produced (see Table 13).

Isotopic Purity of Thiophenol-d.

The amount of isobutane resulting from the abstraction of protium from thiophenol in the deuterated mercaptan was determined by an analysis of the products obtained from the photodecomposition of AIP (0.1 M) in a benzene solution of the thiophenol-d. The results of these experiments are listed in Table 14.

Mass Spectral Analysis of Propane and Propane-2-d.

The mass spectral cracking pattern of propane and propene-2-d show quite intense peaks due to the molecular

Table 12. Photodecomposition of Azoisopropane (0.1 M) in Toluene (9.1-7.8 M) Containing Thiophenol-d (0.11-1.48 M).

Entry	[PhSD] mol/L x 100	non-condensable gases[a] mmolx100	Initial >N=N< mmolx100	Final >N=N< mmolx100	>N(H)-N=< mmolx100	Used >N=N< mmolx100	>H/D[b]	Products, [mmol/mmol >N=N< (used)]x100 >H	>D	⩾	><	PhS(D)	Σ>•/>N=N< (used) x100	% cage	k_d/k_c
1	11.70	7.11	18.8	12.5	0.10	6.20	1.925	74.2	38.5	32.2	27.7	1.14	100.7	61.0	1.20
2	11.90	6.91	18.6	12.2	0.10	6.30	1.890	71.9	38.1	31.2	26.3	1.05	97.4	57.5	1.22
3	48.90	7.32	18.7	11.8	0.048	6.85	0.981	53.2	54.3	29.6	26.0	1.28	95.2	56.9	1.19
4	48.98	7.50	18.8	12.1	0.02	6.67	0.983	55.3	56.3	31.6	28.4	1.88	100.	62.0	1.18
5	97.7	7.79	19.5	12.7	0.12	6.68	0.865	52.2	60.4	32.5	28.9	1.33	102	62.7	1.17
6	98.0	7.67	18.7	11.8	0.15	6.75	0.828	48.3	58.4	30.0	28.3	2.42	97.8	60.7	1.15
7	148.0	8.23	18.6	11.2	0.076	7.32	0.784	46.7	59.5	31.5	27.0	1.87	96.8	60.4	1.23
8	147.8	7.66	18.5	11.9	0.18	6.42	0.784	49.0	62.7	33.4	27.9	1.43	101.0	62.7	1.25

a) Contain N_2, H_2, HD and D_2 (see experimental).

b) Analysis by m/e ions 44/45 (see mass spectral analysis).

Table 13. Photodecomposition of Azoisopropane (0.1 M) in Benzene and Toluene (30°).

Entry	Solvent	non-Condensable gas (N_2) mmolx100	Initial >N=N< mmolx100	Final >N=N< mmolx100	>N-N< mmolx100	Used >N=N<	Products, [mmol/mmol >N=N< (used)] x 100							% Total Unknown	$\frac{\Sigma >\bullet}{>N=N<}$ (used) x 100
							>H	⩾					$(C_6H_5CH_2)_2$		
1	C_6H_6	9.70	18.5	8.54	0.03	9.93	56.4	31.3	28.5	6.50	-	-	-	>7 Products 12.4	75.6
2	C_6H_6	9.90	18.6	8.54	0.03	10.0	57.2	31.3	29.2	6.33	-	-	-	>7 Products 15.7	76.6
3	$C_6H_5CH_3$	10.50	18.2	7.03	0.04	11.1	70.2	29.6	26.2	-	5.20	1.16	4.42	>11 Products 5.1%	79.3
4	$C_6H_5CH_3$	11.01	18.4	6.60	0.04	11.8	70.7	29.3	28.0	-	5.50	1.27	4.43	>11 Products 6.8%	80.4

Table 14. Photodecomposition of Azoisopropane in Benzene in the Presence of Thiophenol-d (0.5 M) at 30°.

Entry	Non-Condensable Gases[a] mmolx100	Initial >N=N< mmolx100	Final >N=N< mmolx100	H | >N-N< mmolx100	Used >N=N< mmolx100	>H/>D[b]	Products, [mmol/mmol >N=N< (used)]x100 >H	>D	⩾	><	PhS-D	Σ>•/>N=N< (Used) x100	[>H]SH/[>D]SD[c]	Average of [>H]SH/[>D]SD
1	7.89	19.0	11.7	0.021	7.28	0.9530	51.2	53.7	30.8	28.8	2.27	96.8	0.3376	
														0.347
2	7.94	19.2	11.8	0.026	7.37	0.9664	52.2	54.0	31.0	28.3	1.97	96.9	0.3561	

a) Contain N_2, H_2, HD and D_2 (see experimental).

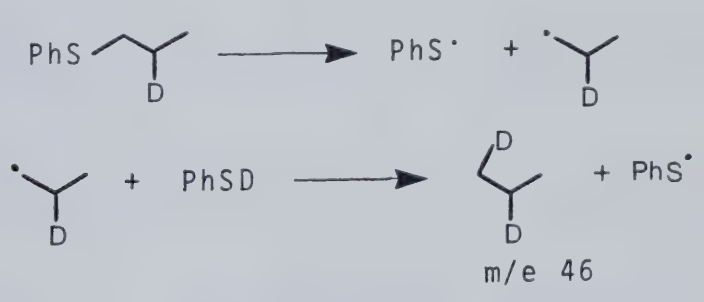
b) Analysis by m/e ions 44/45 (see mass spectral analysis).

c) $\frac{[>H]^{SH}}{[>D]^{SD}}$ = correction factor (f) calculated as:

$$\frac{[>H]^{SH}}{[>D]^{SD}} = f = \frac{[>H]_{Total} - (⩾ + PhS\text{-}D)}{[>D]}$$

ions, m/e 44 and m/e 45. The analyses of the product ratio $[C_3H_8]/[C_3H_7D]$ were carried out by measuring the ratio of the parent M^+ ions at very high resolution (1/25000 atomic mass units). At this high resolution it was possible to show that there was a large contribution to m/e 44 from the fragment M-1 obtained from (C_3H_7D). In each run the ratio of m/e 44 obtained from C_3H_8 and C_3H_6D and the total m/e 44 were measured so that the m/e 44 resulting from the C_3H_8 molecular ion could be measured in an unambiguous manner. It was shown that no other fragment contributes to mass m/e 45. The ratios of [ )—H]/[ )—D] measured in this manner are listed in Table 15.

It was further shown that the component (m/e 45.067329) due to M-1 fragment ion of the compound $C_3H_5D_2$ was absent (Scheme 6). On the basis of this observation, the secondary photolysis of phenyl propyl-2-d sulfide was ruled out.



(SCHEME 6)

Table 15. A Tabulation of the Relative Rates (k_a/k_{SD}), % Cage Reaction, k_d/k_c, Uncorrected, and Corrected Maximum Abstraction from $ArCH_3$ for the Reaction of Azoisopropane.

Entry	Substrate $ArCH_3$	[AIP] mol/Lx100	$[C_6H_5SD]$ mol/Lx100	$[ArCH_3]$ mol/Lx100	>H/>D [a]	>H/>D [b]	k_a/k_{SD} [c] x10^3	% cage [d]	k_d/k_c [e]	Uncorrected [f] maximum abstraction from $ArCH_3$%	Corrected [g] maximum abstraction from $ArCH_3$%
1	$C_6H_5CH_3$	9.35	48.90	875.8	0.981	0.471	26.3	56.9	1.19	22.3	3.47
2	$C_6H_5CH_3$	9.40	48.98	875.8	0.983	0.472	26.4	62.0	1.18	21.8	2.25
3	*m*-$CH_3C_6H_4CH_3$	9.40	49.20	758.1	1.001	0.486	15.8	61.6	1.28	19.7	0.92
4	*m*-$CH_3C_6H_4CH_3$	9.60	49.0	759.2	1.030	0.506	16.3	60.5	1.22	22.6	3.7
5	*p*-$CH_3C_6H_4CH_3$	9.45	48.90	761.4	1.113	0.568	18.3	61.6	1.16	24.4	6.5
6	*p*-$CH_3C_6H_4CH_3$	9.45	49.50	761.4	1.175	0.615	20.0	60.7	1.14	27.1	9.5
7	*m*-$ClC_6H_4CH_3$	9.35	48.90	787.9	0.997	0.483	30.0	61.9	1.24	18.8	0.35
8	*m*-$ClC_6H_4CH_3$	9.35	49.64	783.5	0.971	0.463	29.2	64.5	1.28	16.5	-2.4(0)
9	*p*-$ClC_6H_4CH_3$	9.20	48.87	777.7	1.010	0.492	31.0	60.8	1.28	19.4	1.02
10	*p*-$ClC_6H_4CH_3$	9.20	49.25	775.0	1.101	0.560	35.6	62.1	1.25	20.7	3.3
11	*p*-$CNC_6H_4CH_3$	9.35	48.84	781.7	1.305	0.711	44.4	63.5	1.37	21.6	6.1
12	*p*-$CNC_6H_4CH_3$	9.25	46.24	781.7	1.267	0.869	51.4	62.4	1.37	27.8	13.2
13	*p*-$CNC_6H_4CH_3$	9.30	48.98	775.7	1.193	0.628	39.7	62.9	1.28	23.32	6.3
14	*p*-$C_6H_5OC_6H_4CH_3$	9.40	49.00	526.9	1.921	1.168	108.6	71.8	1.42	21.2	9.7
15	*p*-$C_6H_5OC_6H_4CH_3$	9.40	49.67	524.3	1.822	1.095	103.7	71.7	1.44	22.8	10.4
16	*m*-$C_6H_5OC_6H_4CH_3$	9.3	48.98	532.5	1.514	0.866	79.7	72.1	1.40	18.2	4.4
17	*m*-$C_6H_5OC_6H_4CH_3$	9.45	49.37	532.5	1.525	0.875	81.1	70.6	1.44	16.4	3.1

Footnotes for Table 15 .

a) Analysis by m/e ions 44/45 (see mass spectral analysis).

b) Corrected for thiol impurities from Tables 10 and 14 as,

$$(\succ H/\succ D)_{Corrected} = (\succ H)-f(\succ D)/(\succ D)+f(\succ D).$$

c) Calculated as $k_a/k_{SD} = (\succ H/\succ D)_{corrected}([C_6H_5SD]/[ArCH_3])$, statistically corrected for xylenes.

d) Calculated from Table 10 as, % cage = $\gtrless$ + PhS(D) + $\succ\!\!\prec$.

e) Calculated from Table 10 as, k_d/k_c = ($\gtrless$ + PhS(D)) / $\succ\!\!\prec$.

f) Calculated from Table 10 as, $\succ H$ - ($\gtrless$ + PhS(D)).

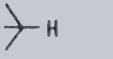
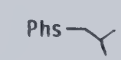
g) Calculated from Table 10 as, ($\succ H$) - [($\gtrless$ + PhS(D)) + f($\succ D$)].

Products of the Reactions of AIB. Material Balance.

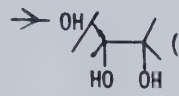
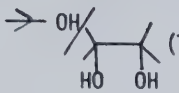
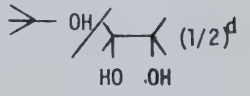
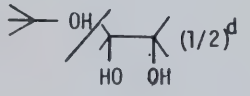
Solutions of AIB (0.1 M) and thiophenol (0.5 M) in chosen solvents were photolyzed to 100% completion. Analyses of the products obtained from these photodecomposition are listed in Table 16. The organic products accounted for from 95 to 100% of the theoretical quantity of tert-butyl radicals produced. The products resulting from the reactions of tert-butyl radicals were isobutane, isobutene, 2,2,3,3-tetramethylbutane, and phenyl isobutyl sulfide. The percentage decomposition was based on the nitrogen collected.

The decomposition of AIB (0.1 M) in solvent benzene and benzonitrile without added thiophenol yielded, besides nitrogen, isobutane, isobutylene, 2,3,3,3-tetramethylbutane, and tert-butylbenzene, and a number of minor products (>4). The minor products were detected by GLC, however they were not identified. The products identified accounted for 94% of tert-butyl radicals produced. In benzonitrile a new product was detected (GLC) which was identified as p-cyano-tert-butylbenzene. Subsequently, using capillary column chromatography, it was shown that this compound contained another minor product which was tentatively identified as o-cyano-tert-butylbenzene in the approximate ratio of 17:1. In addition to these products a number of minor products (>3) were detected (GLC);

Table 16. Photodecomposition of 2,2'-Azoisobutane (0.1 M) in a Variety of Solvents (30°) Containing Thiophenol (0.5 M).

Entry	Solvent	Product N_2 mmol x 100	Products, (mmol/mmol N_2) x 100						
							$\frac{\Sigma \rightarrow \bullet}{N_2}$ x 100	% cage[e]	k_d/k_c[f]
1	$n\text{-}C_7H_{16}$	22.1	136.8	-	38.8	8.47	96.3	47.3	4.57
2	$n\text{-}C_7H_{16}$	22.2	137.0	-	38.9	8.45	96.4	47.3	4.60
3	C_6H_6	19.6	137.4	9.6	36.6	9.10	100.9	55.3	5.08
4	C_6H_6	21.8	130.5	7.4	39.6	9.32	98.0	56.3	5.04
5	C_6H_5Cl	21.8	123.3	14.2	37.6	9.55	97.1	61.3	5.42
6	C_6H_5Cl	21.8	125.5	11.3	37.2	9.16	96.1	57.6	5.30
7	C_6H_5CN	22.0	124.0	37.0	22.0	9.38	100.8	68.4	6.29
8	C_6H_5CN	21.8	123.4	36.8	22.0	9.46	100.5	68.3	6.21
9	$n\text{-}C_{14}H_{30}$[a]	20.9	111.0	29.5	29.8	10.58	95.7	69.9	5.60
10	$n\text{-}C_{14}H_{30}$[a]	20.8	113.2	21.2	39.2	9.87	96.6	70.2	6.12
11	$(C_6H_5)_2O$	21.7	108.2	21.4	48.5	9.48	98.5	79.4	7.37
12	$(C_6H_5)_2O$	21.7	107.3	24.1	44.5	9.72	97.6	78.3	7.05
13	Nujol(L)[b]	20.8	104.4	12.1	56.2	9.90	96.2	78.2	6.90
14	Nujol(L)	20.7	99.1	10.0	61.5	10.87	96.2	82.3	6.57

(continued...)

15	 (1/2)[f]	20.4	95.5	72.4	4.2	11.31	97.3	87.9	6.77
16	 (1/2)[f]	20.8	96.8	72.6	4.8	10.77	97.8	88.2	7.18
17	Nujol(L/H),(1/1)	20.8	100.0	12.7	56.9	10.27	95.1	80.0	6.77
18	Nujol(L/H),(1/1)	20.4	104.3	16.8	55.3	10.27	98.5	82.4	7.02
19	Nujol(L/H),(1/4)	21.0	99.9	20.2	51.0	10.57	96.1	81.8	6.73
20	Nujol(L/H),(1/4)	20.4	98.3	24.6	45.8	9.61	94.0	80.0	7.32
21	Nujol(L/H),(1/4)	20.7	95.7	16.2	58.2	10.41	95.5	94.8	7.14
22	Nujol (H)	21.0	97.0	33.5	45.7	9.96	98.1	89.1	7.95
23	Nujol (H)	21.1	99.6	33.1	45.5	8.74	97.8	87.3	8.99
24	Nujol (H)	20.6	95.2	25.3	50.0	9.78	95.0	85.1	7.70
25	Nujol (H)	20.3	97.1	34.7	41.9	9.50	96.3	86.1	8.06
26	Fluorolube oil	16.7	110.6	15.9	53.7	5.45	95.5	75.0	12.77
27	Fluorolube oil	14.8	105.6	28.5	44.8	5.76	95.2	79.1	12.72
28	 (1/2)[d]	20.2	87.2	80.4	-	10.45	94.2	-	7.69
29	 (1/2)[d]	20.3	86.4	78.3	-	11.42	94.0	-	6.85

Footnotes for Table 16.

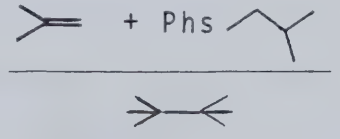
a) Thiol concentration 0.112 M.

b) Nujol (L), light paraffin oil; Nujol (H), heavy paraffin oil; Nujol (L/H), mixture of heavy and light paraffin oil (weight ratios).

c) Mixture of tert-butyl alcohol and anhydrous pinacol (mol ratios).

d) Reactions run without added thiol.

e) Calculations as, % cage = .

f) Calculations as, k_d/k_c =  .

however, these were not identified. The products identified accounted for 82% of the tert-butyl radicals produced (Table 17).

Viscosity Measurement.

The viscosities of the solutions in which the photolysis of AIP and AIB were carried out, are listed in Table 18.

It appears that a large decrease in viscosity of highly viscous solvents is caused by addition of 0.5 M thiol. However the addition of thiol (0.5 M) did not significantly change the viscosity of the low viscosity solvents (see Table 18). The change of viscosities of toluenes (from 4 to 25%) was reported by Tanner et al.,[46] at high concentration of thiol (3 M).

Table 17. Photodecomposition of 2,2'-Azoisobutane (0.1 M) in Benzene and Benzonitrile (30°)

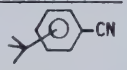
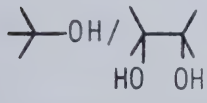
Entry	Solvent	Product $\frac{\text{mmol} \times 100}{N_2}$	Products (mmol/mmol N_2) x 100					% Total Unknown	$\frac{\Sigma \text{ Radicals}}{N_2} \times 100$
									
1	C_6H_6	21.3	89.9	74.4	13.0	1.37	-	> 4 Products 3%	95.8
2	C_6H_6	20.7	85.1	74.2	12.5	1.15	-	> 4 Products 4%	92.7
3	C_6H_5CN	21.7	72.6	63.0	9.60	-	7.2	> 3 Products 3%	81
4	C_6H_5CN	21.4	72.5	64.0	9.67	-	8.4	> 3 Products 3%	82

TABLE 18

Comparison of the Viscosities of Some Solvents With and Without Added Thiophenol

Solvent	η^a	η^b
C_6H_5	0.543	0.526[c]
$\underline{m}$-$MeC_6H_4CH_3$	0.577	0.572[c]
$\underline{p}$-$CNC_6H_4CH_3$	1.410	1.437[d]
$\underline{m}$-$C_6H_5OC_6H_4CH_3$	3.248	3.463[e]
Nujol (L)	12.69	18.74
Nujol (L/H), (1/1)	21.09	36.26
 (1/2)	16.59	27.62

a. Viscosity, cP, of the solvent, containing thiophenol (0.5 M, 30°).

b. Viscosity, cP, of the solvent without thiophenol (30°).

c. Taken from "Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, Ohio, 1976.

d. Taken from F.J. Wright, J. Chem. Eng. Data, 6, 454 (1961).

e. Taken from reference 46.

DISCUSSION

Azoisopropane Decompositions.

Relative reactivities for the decomposition reactions of toluene solutions of AIP. (0.1 M) and thiophenol-d (0.5 M), were calculated from the data, examples of which are listed in Table 15. in the usual manner (Footnote, Table 15). Hammett plots of log k_a/k_a^o vs. the substituent constant, σ,[83] when the values for the m- and p-phenoxytoluenes were excluded, gave a positive rho of (+0.46), (see Table 19 and Figure 1). Using the values for the same substrates reported by Pryor and Davis,[38,39] (Figure 2) a positive rho of (+0.82) was obtained. This discrepancy between the two rho values may be attributable, however, to the difference in the methods used for mass spectral analysis (see Results).

If one examines the data given in Table 15, it is immediately obvious that very little, if any, of the propane results from abstraction from toluene by an isopropyl radical. A large percentage of the isopropyl radicals (~27%, Table 10) abstract deuterium from thiophenol-d. The major portion of the remaining isopropyl radicals appear either to disproportionate to form propene and propane or combine to form 2,3-dimethylbutane (~28%). The propene, its addition adduct

Table 19.[a] Average Relative Rates, k_a/k_a^o, % Cage Reaction and k_d/k_c for Isopropyl Radical.

Entry	Point[b]	Substrate $ArCH_3$	η[c]	Average[d] k_a/k_{SD} x10^3	k_a/k_a^o[e]	log k_a/k_a^o	Average % cage	Average k_d/k_c
1-2	1	$C_6H_5CH_3$	0.543	26.35 ± 0.05	1	0	59.4 ± 2.5	1.18 ± 0.005
3-4	2	*m*-$CH_3C_6H_4CH_3$	0.577	16.05 ± 0.25	0.609	-0.2154	61.0 ± 0.6	1.25 ± 0.03
5-6	4	*p*-$CH_3C_6H_4CH_3$	0.588	19.15 ± 0.85	0.727	-0.1384	61.1 ± 0.5	1.15 ± 0.01
7-8	5	*m*-$ClC_6H_4CH_3$	0.760	29.6 ± 0.4	1.123	0.0505	63.2 ± 1.3	1.26 ± 0.02
9-10	6	*p* $ClC_6H_4CH_3$	0.792	33.3 ± 2.3	1.264	0.1017	61.4 ± 0.6	1.26 ± 0.02
11-13	8	*p*-$CNC_6H_4CH_3$	1.410	45.16 ± 4.1	1.714	0.2340	63.0 ± 0.4	1.34 ± 0.04
14-15	10	*p*-$C_6H_5OC_6H_4CH_3$	3.206	106.2 ± 2.4	4.030	0.6053	71.8 ± 0.05	1.43 ± 0.01
16-17	11	*m*-$C_6H_5OC_6H_4CH_3$	3.248	80.4 ± 0.7	3.051	0.4844	71.4 ± 0.7	1.42 ± 0.02

a) Calculated from the data in Table 15.

b) Point in Figure 11.

c) Viscosity, cP, of the substituted toluenes, containing PhSD (0.5 M).

d) k_a, rate of hydrogen abstraction from $ArCH_3$, and k_{SD}, rate of hydrogen abstraction from PhSD.

e) ka°, rate of hydrogen abstraction from $C_6H_5CH_3$.

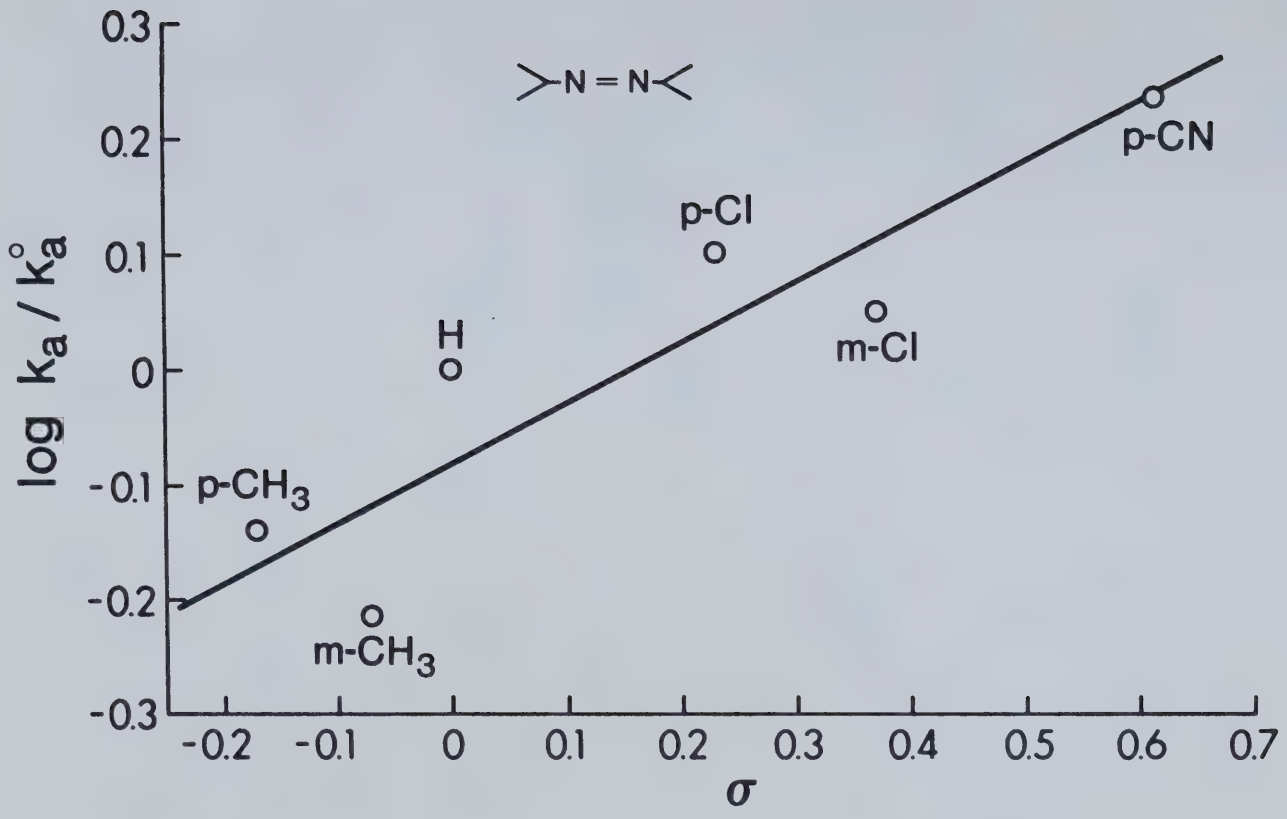


FIGURE 1. A Hammett plot of the apparent log (relative k_a) values for the reaction (30°) of isopropyl radical in substituted toluenes vs. σ.

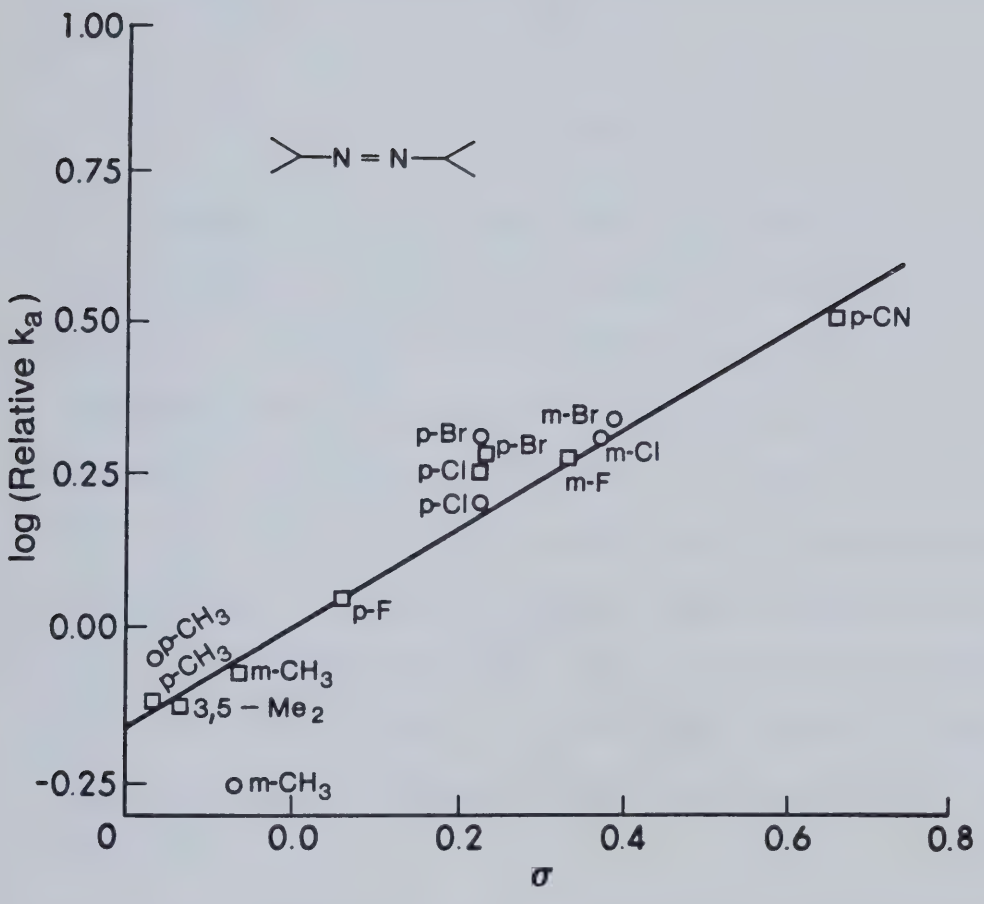


FIGURE 2.* A Hammett plot of log (relative k_a) values for hydrogen abstraction from substituted toluenes by isopropyl radicals at 30° vs. σ. (The symbols, ○, □, correspond to different methods used in the mass spectral analysis of the hydrocarbons).

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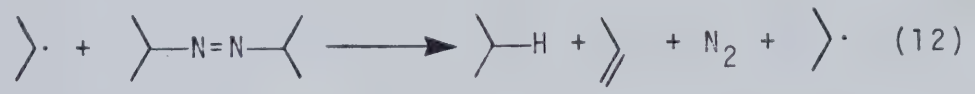
* Taken from reference (39).

(phenyl propyl-2-d sulfide), and an equivalent amount of propane formed by disproportionation account for 72-84% of the isopropyl radicals that do not form deuterated propane (see column headed "uncorrected maximum abstraction from $ArCH_3$", Table 15).

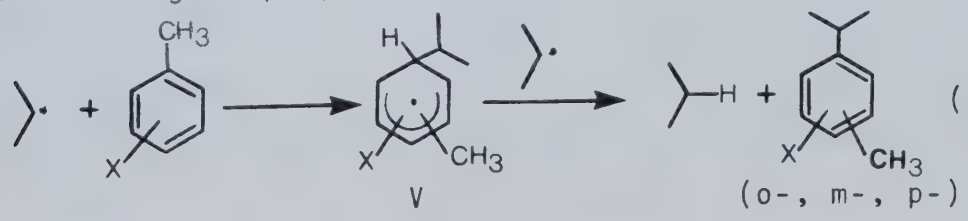
(11)

The disproportionation reaction was shown to be a cage process, since the absolute amount of propene formed (propene plus its addition product phenyl propyl-2-d sulfide) remained essentially constant at concentrations of the scavenger, thiophenol-d, between 0.11 and 1.48 M (Table 12). The results given in this table also demonstrate the absence of induced decomposition, another likely source of propane (equation 12), since the absolute amounts of olefin (plus its addition product) could not remain constant if induced decomposition were an important process.



(12)

Addition of an isopropyl radical to the aromatic ring to give a cyclohexadienyl radical (V) followed by hydrogen abstraction by another isopropyl radical could also give propane (equation 13).



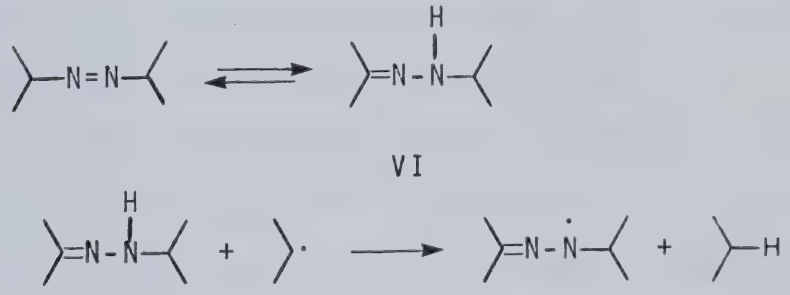
(13)

However, since no o-, m- or p- cymene (X=H) could be detected in the product mixture, reaction 13 can be neglected.

The amount of propane, resulting from the reaction of isopropyl radicals with impurity, thiophenol, present in thiophenol-d, was estimated by carrying out the photodecomposition of AIP (0.1 M) in an inert solvent, benzene, in the presence of thiophenol-d (0.5 M). Since it was shown that reactions 12 and 13 are negligible, then the only reactions which result in the formation of propane are the cage disproportionation of isopropyl radicals and the reaction of isopropyl radicals with impurity, thiophenol. After correction for the amount of propane formed by disproportionation, abstraction from the impurity, thiophenol, amounted to ~34% of the propane-2-d formed in the reaction (for the calculation see the footnote in Table 14). When this fraction of propane was subtracted from the uncorrected maximum amount of abstraction, only 0-13% of the propane formed in any of the reactions which were used for the kinetic analysis could be attributed to benzylic abstraction (Table 15 last column). The correction factor (0.34) for abstraction of protium from the impurity present in the deuterated thiophenol seems too large. However, one should consider the isotope effect for abstraction from thiophenol and thiophenol-d. This isotope effect, k_H/k_D, for the tert-butyl radical was estimated[84] to be

~5. There is, however, no k_H/k_D value available for the isopropyl radical. The purity of thiophenol-d was measured by nmr to be ~97%. Using the correction factor (0.34) and an estimate of k_H/k_D of ~5 for the isopropyl radical, would place the purity of the thiophenol-d at approximately 93%. This value is in fair agreement, within the experimental error, with the nmr analysis.

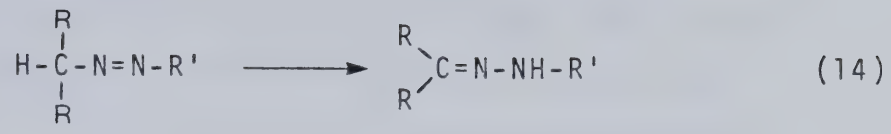
The entry (12) in Table 10 needs some comment. Since the photodecomposition of AIP in p-cyanotoluene produced a significant amount of the rearranged product, isopropylhydrazone, it is possible that the large amount (13%) of hydrogen abstraction was partly due to the hydrogen abstraction from hydrazone (VI), (Scheme 7). It is not clear however, why the reactions carried out in p-cyanotoluene give more hydrazone.



VI

(SCHEME 7)

The rearrangement of secondary azoalkanes has been demonstrated in several cases. For instance it was shown by Kopecky and Gillan[85] that photodecomposition



(14)

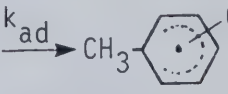
of 1-1'-diphenyl-1-methylazomethane resulted in the almost exclusive formation of the corresponding hydrazones. Thermolysis of this azo compound in presence of n-butanethiol produced small amount of unsymmetrical azine, acetophenone benzaldehyde azine, (C_6H_5-$\overset{CH_3}{\overset{|}{C}}$=N-N=CH$C_6H_5$). Formation of azine has also been reported by Kooyman[86] to be a product formed during the decomposition of 1,1'-diphenazoethane in presence of octanethiol. It has been suggested[80] that these dehydrogenations may be initiated by hydrogen abstraction from the azo compounds by thiyl radicals. It was also shown by Paterson and Ross[87] that the thermal rearrangement of 1,1'-diphenazoethane to the corresponding hydrazone could be catalyzed by acid.

It is not surprising that isopropyl radicals readily react with thiophenol in preference to toluene, or that in fact they undergo bimolecular reaction rather than competitive abstraction from toluene. Chain transfer data for a variety of structurally different polymer radicals invariably show that they react with thiols >10^4 times faster than with toluenes,[88] any values of relative reactivity much different from this would be suspect. A comparison of the rates of reaction

with toluene of several radicals (i.e., poly vinyl acetate radicals, 5 $M^{-1}S^{-1}$ at 60°, or polystyryl radicals,[89] 1.8 x 10^{-3} $M^{-1}S^{-1}$) with the rates for the bimolecular self termination of simple alkyl radicals (2 x 10^{9} $M^{-1}S^{-1}$),[90] clearly demonstrates that only at very low rates of radical production should the abstraction reaction effectively compete.

A further indication that in this system benzylic hydrogen abstraction is a negligible reaction comes from the results of the photodecomposition of AIP in neat toluene. The reaction yielded isobutylbenzene (5.5%), isopropyltoluene (~1.2%) and bibenzyl (~4.4%) arising presumably according to the following reactions (Scheme 8).

i) $(CH_3)_2CH\text{-}N{=}N\text{-}CH(CH_3)_2 \xrightarrow{h\nu} 2(CH_3)_2\dot{C}H + N_2$

ii) $(CH_3)_2\dot{C}H + C_6H_5CH_3 \xrightarrow{k_{ad}}$  $\longrightarrow (CH_3)_2CHC_6H_4CH_3$ (o-,m-,p-)

iii) $(CH_3)_2\dot{C}H + C_6H_5CH_3 \xrightarrow{k_a} (CH_3)_2CH_2 + C_6H_5\dot{C}H_2$

iv) $C_6H_5\dot{C}H_2 + C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$

v) $C_6H_5\dot{C}H_2 + (CH_3)_2\dot{C}H \longrightarrow C_6H_5CH_2CH(CH_3)_2$

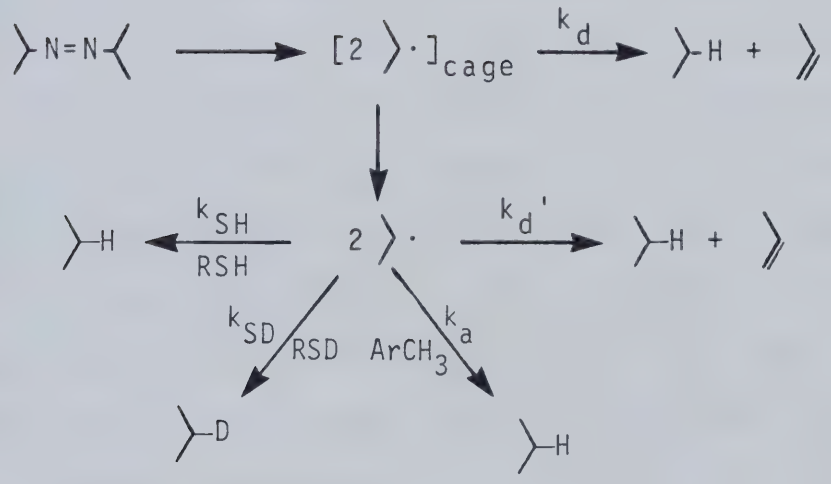
(SCHEME 8)

Since all products arise from the reaction of radicals formed from the bimolecular reaction of an isopropyl radical and a toluene molecule, both the benzyl and the cyclohexadienyl radicals and their products should be formed in a definite ratio regardless of the number of isopropyl radicals which are scavenged. When thiophenol was added to the reaction mixture no bibenzyl, isopropyltoluene or isobutylbenzene were detected (GLC). The absence of bibenzyl and isobutylbenzene would be expected since it would have to be produced from the coupling of two radicals in the presence of an efficient scavenger, thiophenol. However, if the abstraction from toluene had taken place then a detectable amount of isopropyltoluene should have been detected since the addition product and the coupling products are formed in a ratio of ~0.13 (k_{ad}/k_a). Since a material balance is obtained, and no detectable amount of addition product was formed it follows, therefore, that no appreciable abstraction from toluene had taken place. The validity of this argument, however, does depend on the reasonable assumption that the addition reaction is irreversible under the reaction conditions.

As disproportionation has been shown to be the major source of propane in the reaction of isopropyl radicals in toluenes (similar to tert-butyl radicals)[46]

a reexamination of the kinetic assumptions made by Pryor[39] is once more necessary. A similar rate expresion (15) can be derived for the appearance of propane and propane-2-d using the equations shown in Scheme 9;

$$\frac{d[C_3H_8]/dt}{d[C_3H_7D]/dt} = \frac{k_a[ArCH_3]}{k_{SD}[RSD]} + \frac{k_{SH}[RSH]}{k_{SD}[RSD]} + \frac{k_{dec}f_c[initiator]}{k_{SD}[C_3H_7\cdot][RSD]} + \frac{k_d'[C_3H_7\cdot]}{k_{SD}[RSD]} \quad (15)$$



(SCHEME 9)

The last term in equation 15, i.e., disproportionation of the radicals out of the cage was ruled out on the basis of the observation that the absolute amount of olefin plus its addition product, did not change in reactions run with increasing thiol concentration. This

is a valid assumption which was also pointed out by Pryor.[39] However the third term in the right hand side of equation 15, i.e., the cage disproportionation term, has now been found to be the major term even though it has been stated to be negligible by Pryor.[39] As in the case of tert-butyl radicals, it was this incorrect assumption that allowed Pryor to integrate the above expression and to use the integrated form to obtain kinetic values for k_a/k_{SD}.

All, or nearly all, of the propane formed in the reaction can be attributed to the cage disproportionation (after a correction for abstraction from thiophenol). Since, the ratio of rate constants, k_a/k_{SD}, obtained by determining the ratio of products, $[C_3H_8]/[C_3H_7D]$, varied in a systematic manner from substrate to substrate, as in the case of tert-butyl, it was concluded that the viscosity of the solvent was controlling the absolute amount of disproportionation, and hence the propane formed. Accordingly, a plot of solvent fluidity, $1/\eta$, vs. 1/cage yield or 1/[olefin], gave a nearly linear correlation (Figures 3 and 4). Furthermore, according to Noyes' model the fraction of the cage reaction which takes place in the cage should correlate with the fluidity of the solvent. Thus, a plot of the relative reactivity given in Table 19, uncorrected for disproportionation, but corrected for the thiophenol impurity in the thiophenol-d, vs. the fluidity of all of

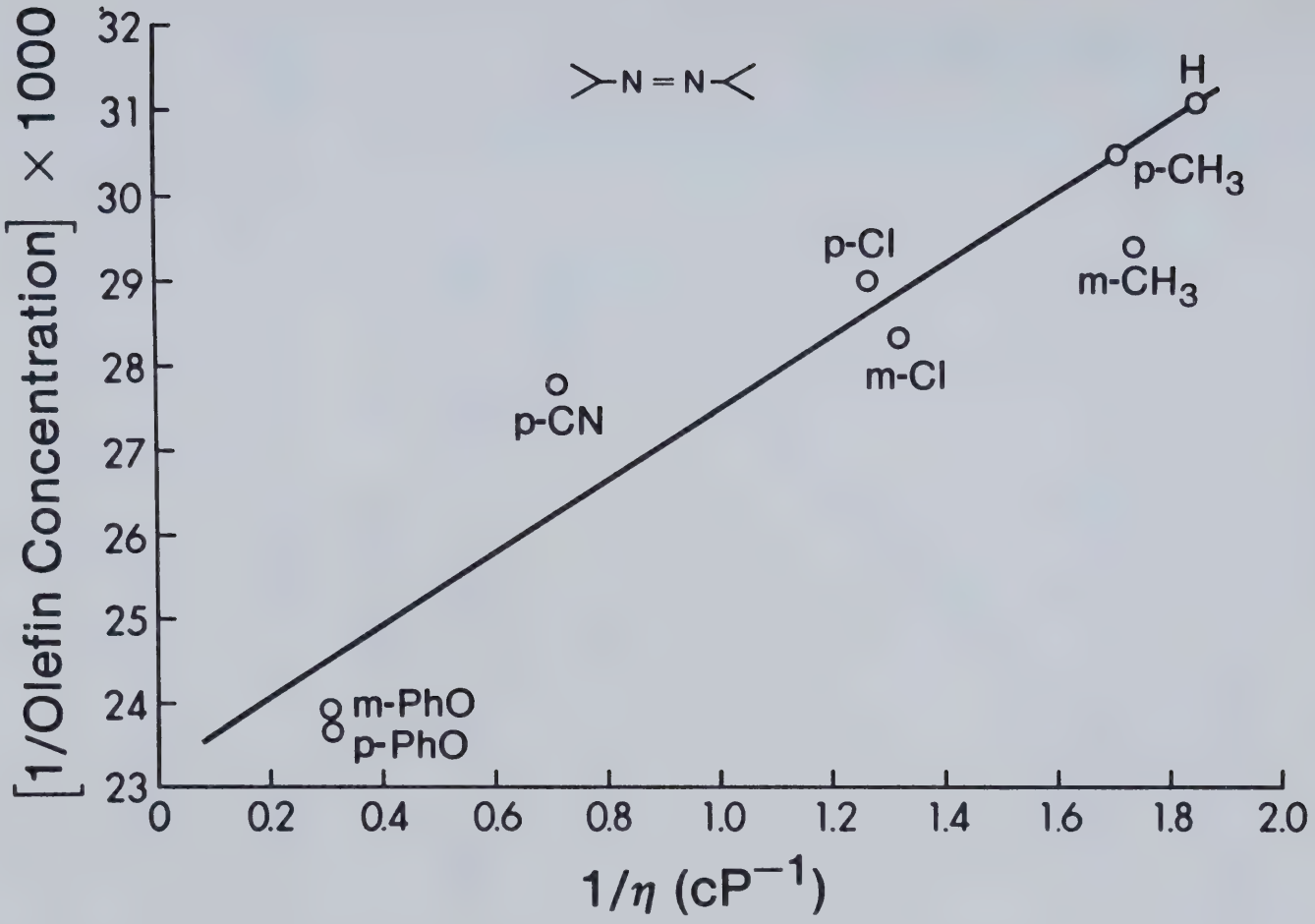


FIGURE 3. Plot of the fluidity. 1/η, of the solvents used vs. 1/olefin concentration, for the formation of propylene formed in the photodecomposition of azoisopropane with added PhSD (0.5 M).

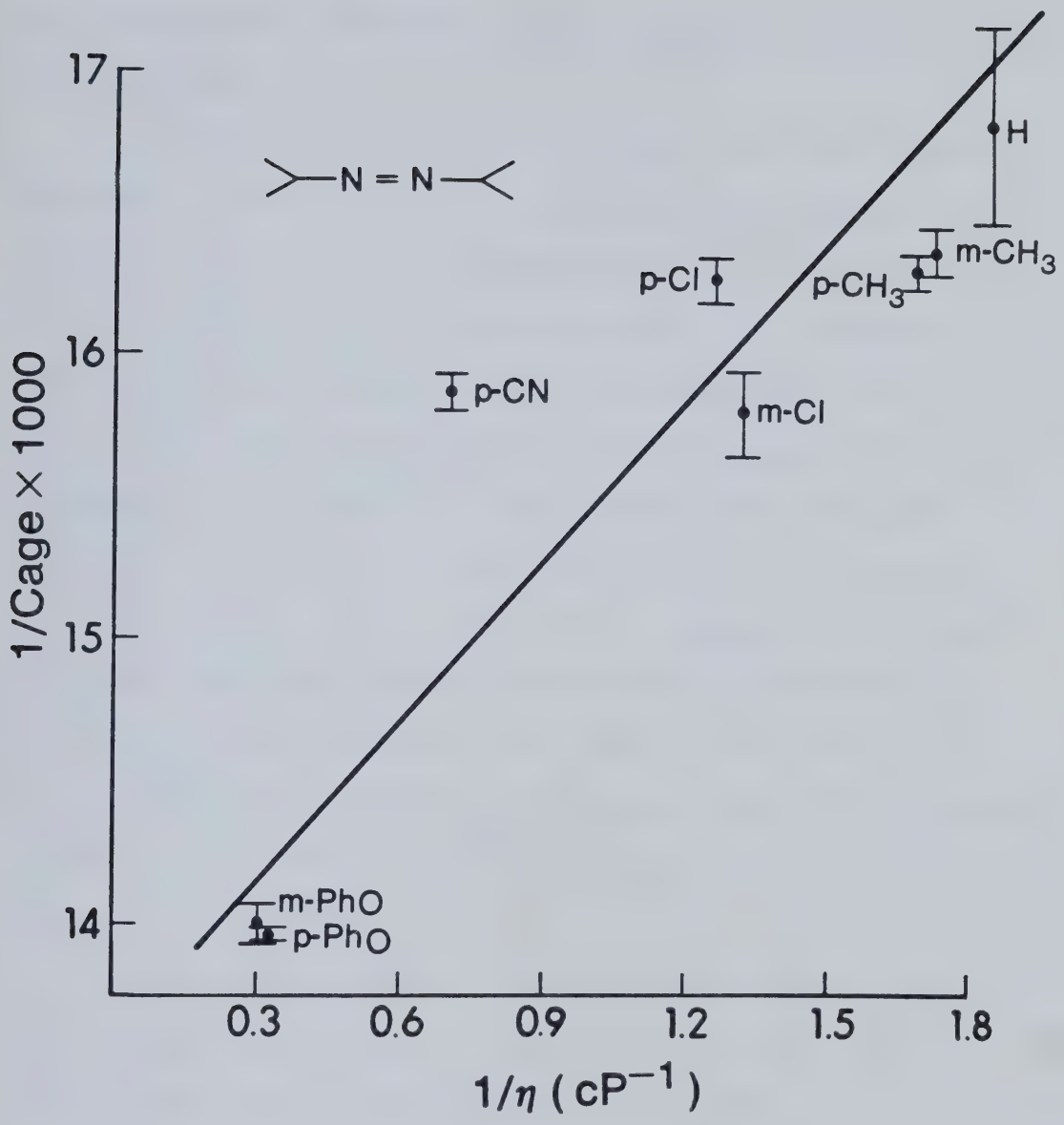


FIGURE 4. Plot of the fluidity, $1/\eta$, of the solvents used vs. the cage efficiency, 1/c, for the formation of the cage products formed in the photodecomposition of azo-isopropane with added PhSD (0.5 M).

the substrates (solvents) gave a relatively good correlation (Figure 5).

The observed positive rho values for alkyl radicals have been interpreted by Zavitsas as being due to the electrophilic character of these radicals, i.e., due to the addition of radicals to the aromatic ring. However, when photodecompositions of AIP and AIB were carried out in toluenes and benzenes in the presence of thiol scavenger, no product of ring addition was detected (Tables 11 and 16). Furthermore the plot of fluidity, $1/\eta$, of arenes vs. 1/cage yield, was similar to that obtained for the toluenes (see Table 20 and Figure 6). It should be pointed out that, even in the absence of thiol, the ring addition of isopropyl radicals to benzene (~6%), or toluene (~1.2%) is a minor pathway (see Table 13).

It was clear at this stage that the results of the photodecomposition of azoisopropane were very similar to that of the tert-butyl radical.

Viscosity Dependence of k_d/k_c.

The photodecomposition of 2,2'-azoisobutane (0.1 M, 30°) was carried out in a variety of solvents which contained thiophenol (0.5 M). The viscosity of these solutions ranged from (0.5-808 cP). The products and material balance are listed in Table 16.

Since the tert-butyl radicals generated in the

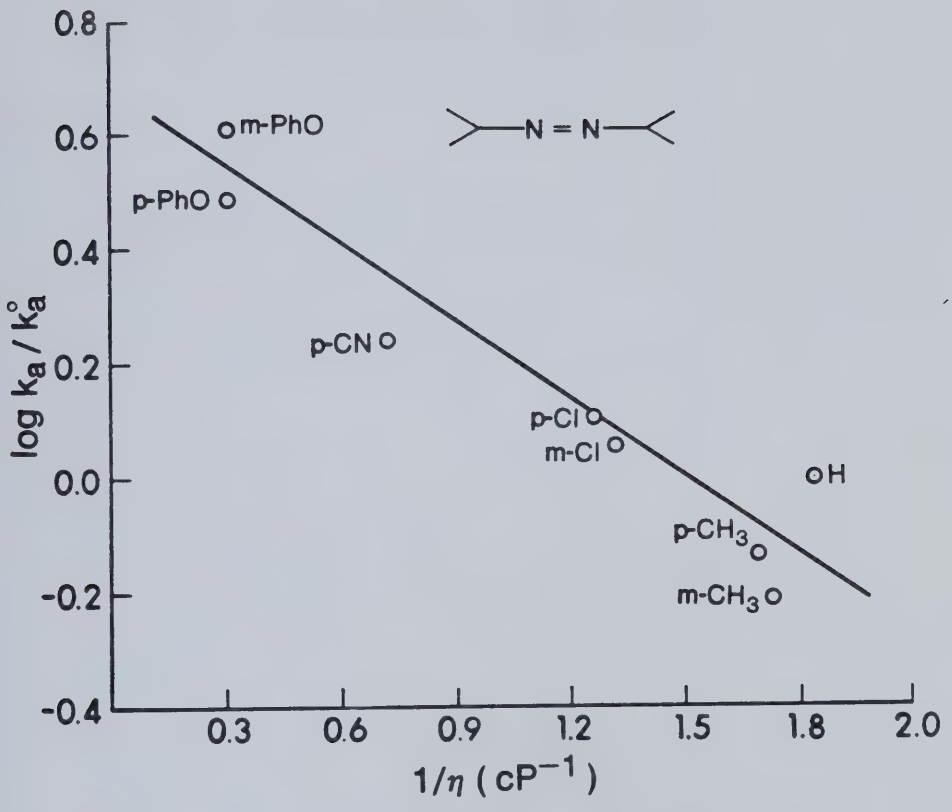


FIGURE 5. Plot of the apparent log (k_a/k_a^o), corrected for abstraction from thiophenol, vs. $1/\eta$ for the photodecomposition reaction of azoisopropane with added PhSD (0.5 M).

Table 20.[a] Average Values of % Cage Reaction and k_d/k_c for Isopropyl Radical

Entry	Point[b]	Solvent	η[c]	% cage	k_d/k_c
1-2	1	$C_6H_5CH_3$	0.543	58.4 ± 0.8	1.2 ± 0.02
3-4	3	C_6H_6	0.587	60.9 ± 1.3	1.15 ± 0.02
5-7	7	C_6H_5CN	1.13	61.9 ± 0.6	1.36 ± 0.03
8-9	9	$(C_6H_5)_2O$	3.07	67.9 ± 2	1.44 ± 0.02
10-11	12	Nujol(L/H),(1/1)	21.1	71.5 ± 2.8	1.24 ± 0.01
12-13	13	Nujol(L/H),(1/2)	27.5	73.4 ± 3	1.25 ± 0.02
14-15	14	Nujol(H)	43.8	71 ± 1.2	1.32 ± 0.005

a) Calculated from the data in Table 11.

b) Point in Figure 11.

c) Viscosity, in cP.

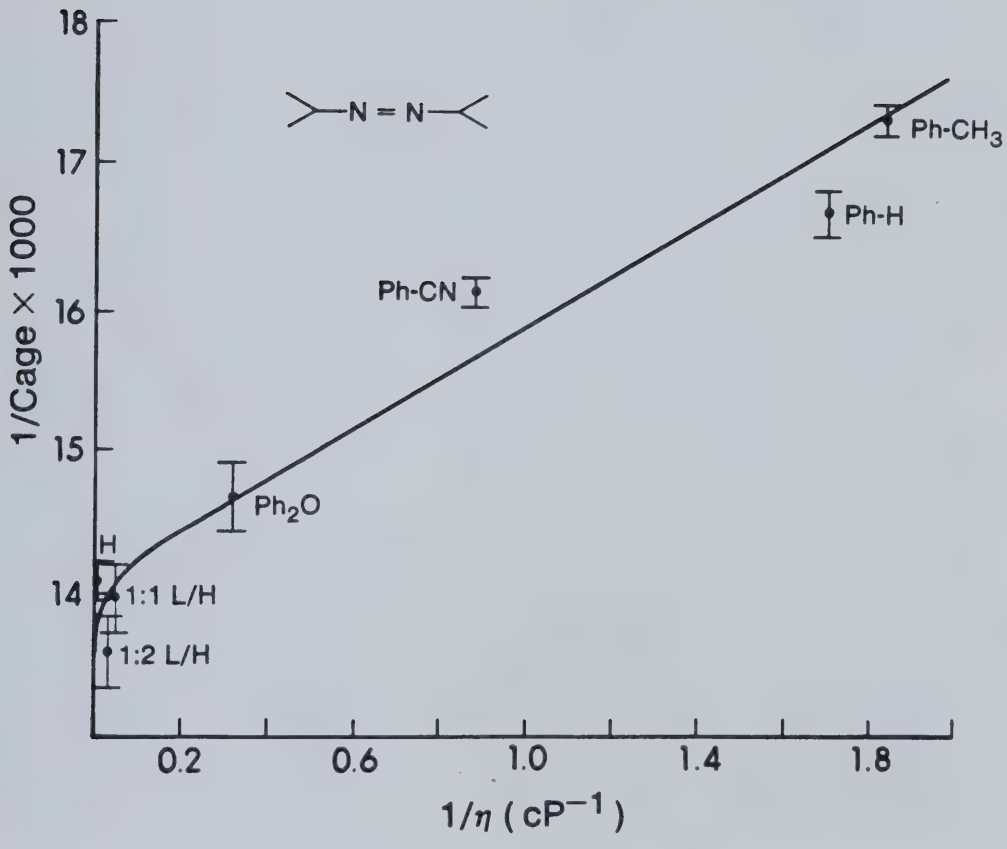
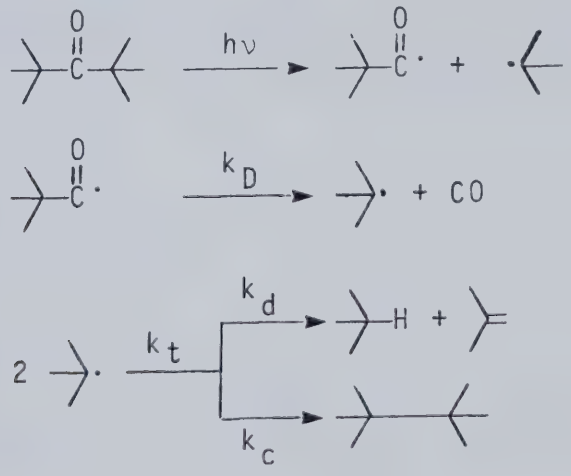


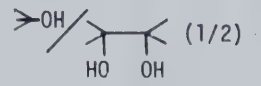
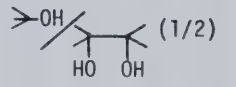
FIGURE 6. Plot of the fluidity, 1/η, of the solvent used vs. the cage efficiency, 1/c, for the formation of the cage products formed in the photodecomposition of azoisopropane with added PhSH (0.5 M).

reaction have been shown[46] either to undergo cage termination reactions or to be scavenged by thiophenol, then combination and disproportionation products are the result of the reaction of geminate caged pairs. The relative rates of disproportionation vs. combination of these pairs of tert-butyl radicals are calculated from the product distribution and are listed in Table 21. The previous interpretation of the factors which controlled the ratio of disproportionation to combination, k_d/k_c, was presented in the Introduction section. None of these explanation, with the exception of Fischer's model, could adequately rationalize the dependence of k_d/k_c on the media. Fischer generated tert-butyl radicals by photolysis of di-tert-butyl ketone. He had previously shown,[91] using carbon tetrachloride as scavenger, that radical self termination was only due to the reaction of encounter pairs (Scheme 10).



(SCHEME 10)

Table 21.[a] Average Values of k_d/k_c and % Cage Reaction for tert-Butyl Radical.

Entry	Point	Solvent	η[b]	Average k_d/k_c	Average % cage
1-2	1	$n\text{-}C_7H_{16}$	0.384	4.58 ± 0.01	47 ± 0.0
3-4	2	C_6H_6	0.587	5.06 ± 0.02	56 ± 0.5
5-6	3	C_6H_5Cl	0.713	5.36 ± 0.06	59 ± 1.8
7-8	4	C_6H_5CN	1.13	6.25 ± 0.04	68 ± 0.0
9-10	5	$n\text{-}C_{14}H_3O$	1.81[c]	5.86 ± 0.26	70 ± 0.1
11-12	6	$(C_6H_5)_2O$	3.07	7.21 ± 0.16	79 ± 0.5
13-14	7	Nujol(L)	12.6	6.73 ± 0.16	80 ± 2
15-16	8	 (1/2)	16.6	6.97 ± 0.20	88 ± 0.1
17-18	9	Nujol(L/H),(1/1)	21.1	6.89 ± 0.13	81 ± 1.2
19-21	10	Nujol(L/H),(1/4)	32.9	7.06 ± 0.22	82 ± 1.7
22-25	11	Nujol(H)	48.6	8.17 ± 0.40	87 ± 1
26-27	12	Fluorolube oil	80.8	12.8 ± 0.08	77 ± 2
28-29	13	 (1/2)	27.6[d]	7.27 ± 0.42	-

a) Calculated from the data in Table 16.

b) Viscosity, cP, of the solvent, containing, thiophenol (0.5 M), (30°).

c) Thiol concentration 0.112 M.

d) Reaction run without added thiol.

Fischer[73] developed an elegant collision model which accounts for the viscosity dependence of the k_d/k_c ratios. The model assumes that, while a great majority of the collisions of encounter pairs are unproductive, the distribution of product from the successful (i.e., product forming) reactions is controlled by the anisotropic reorientation of the radicals which react in a newly formed solvent cage.

A qualitative description of the model assigns potential collision surfaces to a planar (or rapidly inverting pyramidal) radical. Figure 7 shows two projections A and B of a space filling model of a tert-butyl radical with its nine hydrogen atoms (white spheres), three methyl carbon atoms (black), and the central carbon atom (striped). The axis denoted by || is the symmetry axis of the half-occupied p-orbital. The surface, depicted as an oblate ellipsoid can be pictured as having nonreactive, N, zones (~90%) reactive, C, zones leading to combination (~5%), and reactive, H, zones leading to disproportionation (~5%) (Figure 8). Reorientation of the radical, relative to the C zone of its reaction partner leads to either combination (CC configuration) or disproportionation (CH configuration) products, whereas, the CN configuration leads to no product (see Figure 8). According to this model reorientation about || axis affects only H and N zones and can only lead to disproportionation products. This

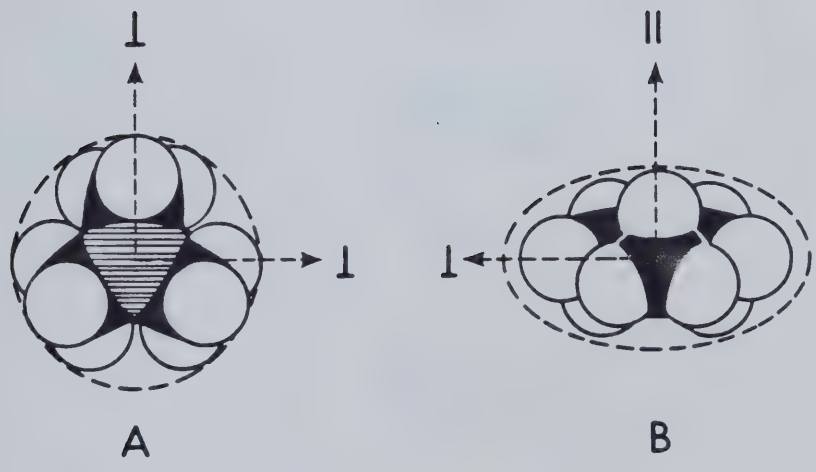


FIGURE 7.* Two projections of a space-filling model of a planar tert-butyl radical.

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* Taken from a drawing in reference 73.

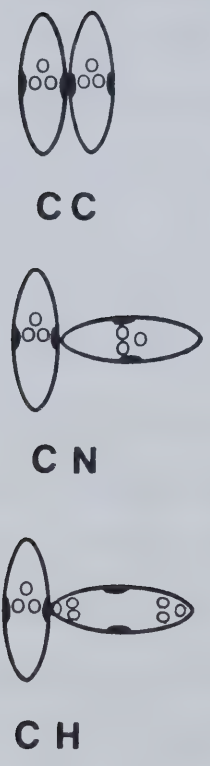


FIGURE 8. Pair configurations of colliding tert-butyl radicals.

reorientation process is not greatly affected by the solvent viscosity since only a minimal amount of solvent is displaced by this motion. Reorientation about $\perp$ axis, which leads to combination products, is strongly coupled to the viscosity of the medium, since, because of the proposed shape of the radical, this motion displaces a maximum amount of solvent. The model predicts a linear relationship between k_d/k_c and viscosity, as has been observed by Fischer.[73]

The data presented in Table 21 was obtained from geminately formed tert-butyl radicals and that of Fischer was obtained from encounter pairs (Table 9). The possible differences between the reaction of encounter and geminate pairs have been discussed in terms of several factors:

The stereochemistry or relative orientation of one radical to the other has been considered.

Kopecky and Gillan[85] and Greene,[67] have independently shown that in the decomposition of optically active azoalkanes, such as, (-)-(S)-1,1'-diphenyl-1-methylazomethane and SS-(-)-1,1'-diphenylazoethane, some retention of configuration does attend the geminate combination of the α-phenylethyl radical with itself or with neighboring benzyl radicals. The analysis of the products, gave the ratio of the rotational rate constant, k_r, to the rate constant for combination, k_c of $k_r/k_c = 15$[67] at 180° and $k_r/k_c = 16$ at 110°.[85]

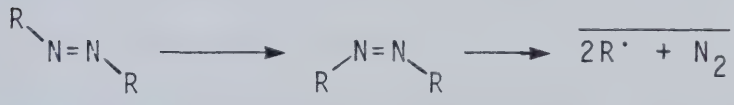
The observation that some geometric memory is maintained, clearly demonstrates, that for these radicals at least, encounters leading to products, do not have a random orientation.

These results suggested that, the caged pair should behave differently from the colliding pair. The same conclusion was drawn by Bartlett and McBride[49] based on the experimental evidence which showed k_d/k_c in the solid phase for 2-phenyl-3-methyl-2-butyl and cumyl radicals to be considerably different from the results obtained in solution.

The radicals produced in photochemical reaction possess excess energy which must equilibrate thermally if there is time prior to reaction. For geminate cage radicals, since there is less time to dissipate the excess energy, it is expected that there could be some difference in the k_d/k_c ratios obtained from geminate and encounter radical pairs. However identical k_d/k_c values have been obtained for both cage and bulk products produced from the decomposition of azocumene,[63] azocyclohexane[92] and ethyl radicals.[68] These observations have shown that k_d/k_c ratios are independent of the excess energy possessed by these radicals at the instant of formation.

Differences in the ratios of combination/disproportionation associated with the spin multiplicity of the radical pairs have not been observed.[93]

Only the first of these factors can be important in the analysis of the solution phase reactions of tertiary butyl radicals occurring between both encounter and geminate pairs, if Fischer's model (which has been corrected statistically for spin) is used, and if the photodecomposition of 2,2'-azoisobutane proceeds by thermal decomposition subsequent to photochemical isomerization of the trans-azo compound to its cis-isomer.[94]



(16)

Azoalkanes can exist in either the cis or trans configuration, but conversion of one form to the other, when both groups are alkyl, can generally be effected photochemically.[94] An exception to this generalization of bridgehead azoalkanes. For example trans-di-1-adamtyldiazene and trans-di-1-norbornyldiazene were thermally isomerized to the corresponding cis isomers.[94c] It has also been shown[95] when one or both groups are aryl, thermal isomerization of cis to trans is a facile

process. The cis isomer of AIB is very unstable and therefore difficult to isolate and has been prepared in situ by irradiation of the trans isomer.[94] The cis isomer of AIP, likewise, was prepared[96] by photolysis of the trans isomer, however, it was stable and could be isolated using GLC.

As previously observed by Tanner et al.[46] for the AIB/PhSD system, a linear relationship between the fluidity of the solvent, $1/\eta$, and the cage efficiency, $1/c$, of the radicals was obtained over the range of viscosities covered by the study carried out in solvent toluenes (0.5-3.5 cP).[46] However, at very high viscosities (12.6-808 cP) some deviation from this behavior is observed (Figure 9).

Photodecomposition of AIP in the presence of thiophenol in solvents with viscosities ranging from (0.5-43.8 cP) also showed a viscosity dependence of cage efficiency, $1/c$ vs. fluidity, $1/\eta$, (see Figure 6). Non-linearity at very high viscosity is evident in this system as well. Deviation from linearity in the plot of $1/c$ vs. $1/\eta$, at low viscosities has been observed in many systems.[97] The upward curvature at low viscosity, in the photodissociation of iodine,[98] was greater than that predicted by Noyes' model, in spite of calculations which included the $(1/\eta)^2$ term. Koenig[99] showed that the square-root of fluidity,

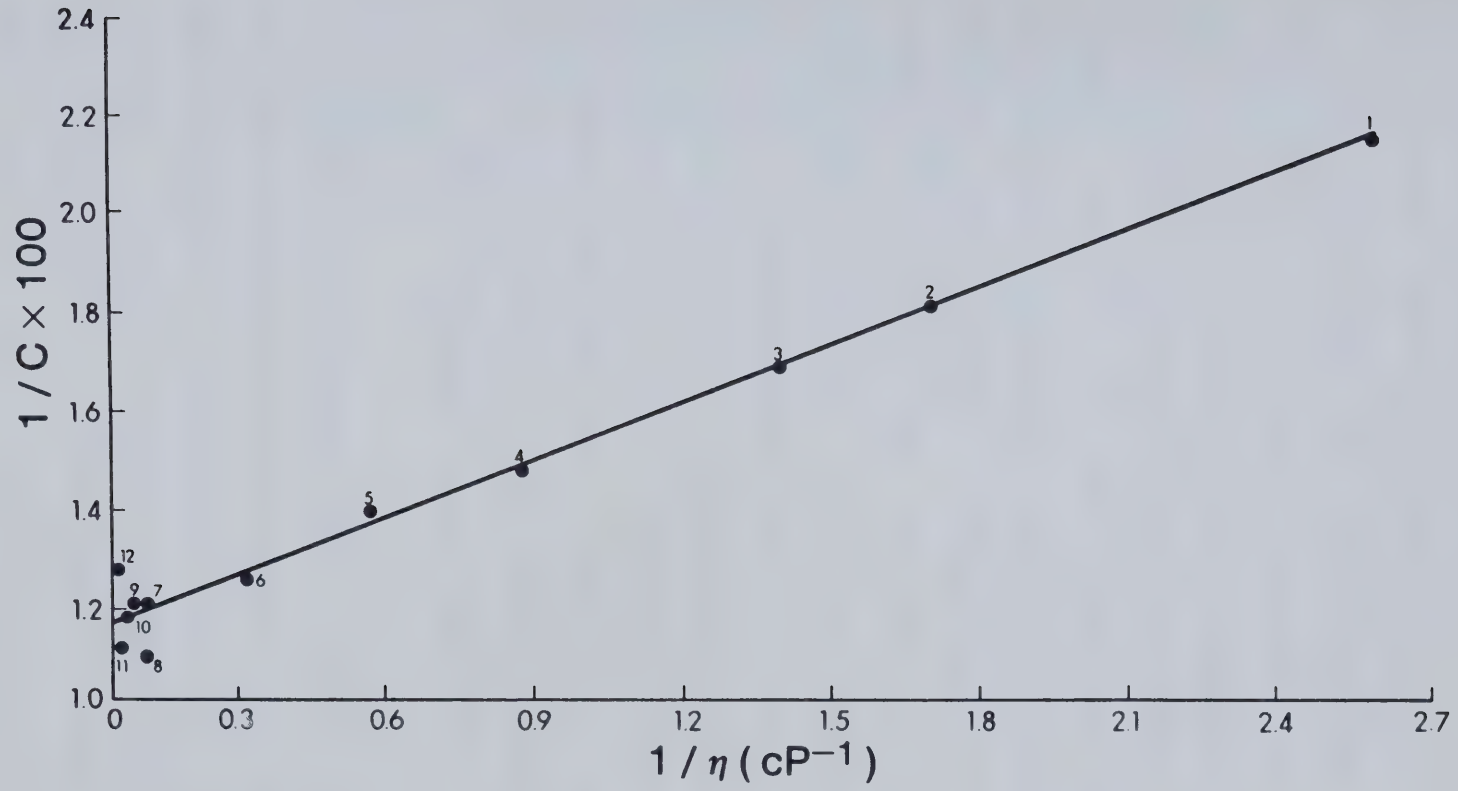
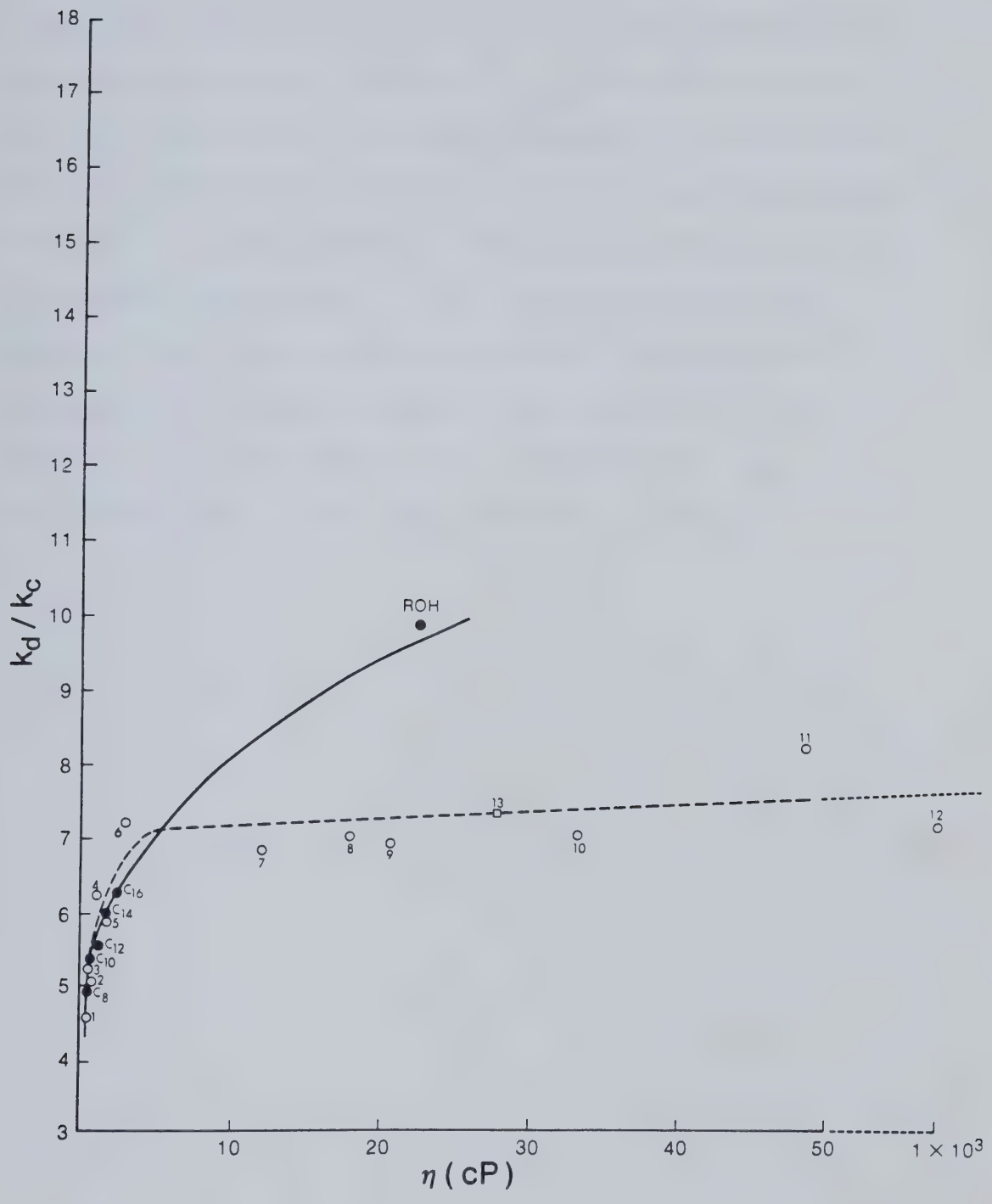


FIGURE 9. Plot of the fluidity, 1/η, of the solvent used vs. the cage efficiency, 1/c, for the formation of the cage products formed in the photodecomposition of 2,2'-azoisobutane. (Numbers correspond to the solvents listed in Table 21).

correlated with the reciprocal of cage efficiency in decomposition of acetyl peroxide. He also observed a strong upward curvature at low viscosity in this system.

In the decomposition of di-tert-butyl peroxyoxalate, in solvents with a viscosity ranging from 0.2-80 cP, a plot of the reciprocal of the di-tert-butyl peroxide yield, versus the fluidity of the solvents gave a sigmoid curve.[97a] In this system, the high viscous solvents were obtained by dissolving different quantities of Nujol in hydrocarbon solvents such as isooctane. Szwarc[97c] has argued that this type of observation is a reflection of the type of solvents used and the correlation of the experimental data with one or another power of viscosity is not a very powerful argument for any particular model. It is, therefore, concluded that at present time there is no model, which can adequately explain the downward or the upward curvature in a plot of the cage efficiency versus the fluidity of the solvents.

A comparison between the effect of viscosity upon the disproportionation-combination ratio observed for encounter pairs[73] and geminate pairs of tertiary butyl radicals, is seen in Figure 10. The k_d/k_c values, at 30° for encounter pairs, were obtained by extrapolation, from the plot of the reported k_d/k_c ratios versus temperature. Over the range of viscosity, 0.48 to 2.67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k_d / k_c
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C_{14}
C_{12}
C_{10}
C_8
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11
12
13
10
20
30
40
50
1×10^3
η (cP)

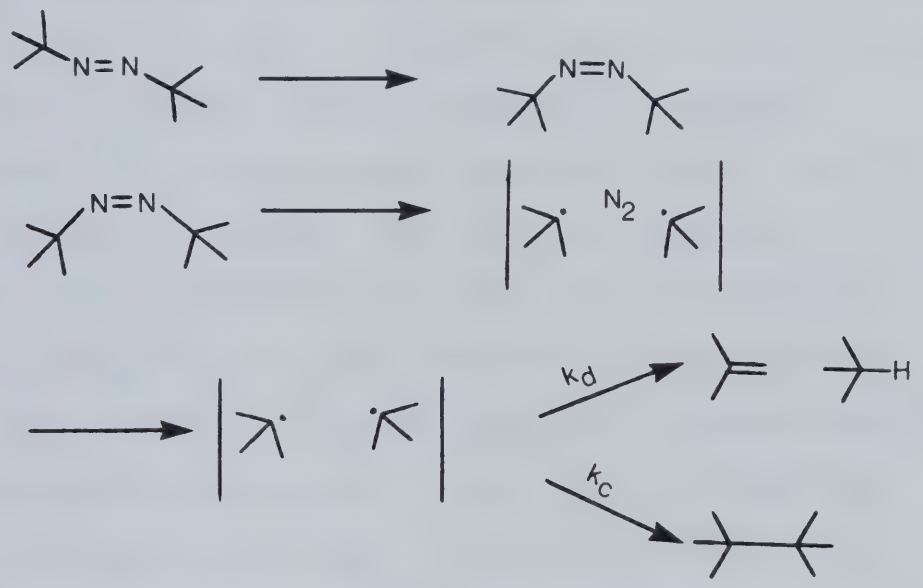
FIGURE 10.

FIGURE 10. Plot of the ratio of cage disproportionation to combination rate constant, k_d/k_c, as a function of solvent viscosity η. (The open symbols ○, □, correspond to the points listed in Table 21 for the photodecomposition of 2,2'-azoisobutane. The closed circles, ●, are the values taken from ref. 73 (extrapolated to 30°) obtained for the photodecomposition of di-tert-butyl ketone in the solvent listed: C_8, n-octane; C_{10}, n-decane; C_{12}, n-dodecane; C_{14}, n-tetradecane; C_{16}, n-hexadecane; ROH, (1/2) $(CH_3)COH/((CH_3)_2COH)_2$).

cP, the viscosity dependence of the k_d/k_c ratios found for the encounter pairs is almost identical to those obtained in this study of the reaction of geminate pairs. The similarity between the values obtained at low viscosities suggests that the tert-butyl radical pairs generated from the azo photolysis are formed with sufficient rotational energy to appear to be randomly oriented. The products from the reaction of these geminate pairs are controlled, as are the products from the encounter pairs, by anisotropic re-orientation.

There is a marked deviation from linearity of Fischer's value for k_d/k_c vs. η obtained for reactions carried out in 1:2 mixtures (η^{30} = 27.6) of tert-butyl alcohol/pinacol (Figure 10, ROH, ●). The termination rate constant ($2k_t$) for tert-butyl radicals in alcoholic solvents was found to be a non-linear function of both the reciprocal temperature (1/T) and the temperature fluidity relationship (T/η). The deviation from the predicted value was attributed, by Fischer to the nonlinear relationship observed between macroscopic viscosity and the motion of the small tert-butyl radicals in alcoholic solvents. However, for non-alcoholic solvents such as hydrocarbons, $2k_t$ was shown to be a linear function of both (1/T) and (T/η). Over the range of viscosities from 12-808 cP the ratio

of termination constants does not increase significantly (Figure 10, pts. 7-12), and it appears that the free reorientation model fails to predict the value of k_d/k_c. The kinetic behavior of the geminate pairs in the very viscous solvents suggests that a random array of collisional orientations is not available to the radical pairs at birth. Although anisotropic reorientation must affect the ratio of rate constants in the more viscous media, the non-random orientation of the radicals upon formation appears to be more biased towards a relatively larger amount of combination (Scheme 11).



(SCHEME 11)

In order to support this explanation, the photodecomposition of AIB was carried out in mixed alcohols, 1:2, tert-butyl alcohol/pinacol with and without added thiophenol (Figure 10, pt. 8 and 13). Under these

conditions ~80% of the combination-disproportionation reaction can be estimated (Table 21, pt. 8 and 13) to occur within the cage, while <20% of the products would arise from cage escape radicals. The major difference between the reactions reported by Fischer[73] (Figure 11, pt. ROH, ●) and the cage reaction (Figure 10, pt. 13) is that the products are formed from oriented geminate radicals; i.e. the ratio of rate constants agrees with the values predicted for the other highly viscous solvents and deviates markedly from the value obtained from the reaction of encounter pairs.

Our results clearly demonstrate that in low viscous solvents, tert-butyl radicals generated by photodecomposition of azoisobutane (geminate pairs) have enough rotational energy that they are randomly oriented as encounter pairs. This fact is reflected in the similarity of k_d/k_c for geminate and encounter tert-butyl radicals. However, Kopecky[85] and Greene's[67] findings on the thermolysis of the optically active azo compound (1,1'-diphenyl-1-methylazomethane) show that some memory may remain in the asymmetric radical after its formation (k_r/k_c = 16), i.e., α-phenylethyl radicals are not completely randomly oriented. It is speculated that the method of optical activity measurement is more sensitive and one can measure such a small difference between rotation and combination. However

we would not be able to detect this difference by measuring the disproportionation-combination ratio, since this small difference (1/16) would not have changed k_d/k_c significantly. More likely this difference between our system and Kopecky and Greene's systems could be explained by considering that the tert-butyl radical is a smaller molecule than α-phenylethyl radical and probably, can randomly be reoriented much more easily.

Disproportionation-combination ratios were also measured for isopropyl radicals in solvents with viscosities ranging from (0.5-43.8 cP), (Table 20). Since isopropyl radicals are generated from azoisopropane, the values of k_d/k_c in Tables 19 and 20 represent disproportionation-combination ratios for geminate radical pairs. No values of k_d/k_c are available for this radical obtained from encounter pairs. Disproportionation-combination ratios increase with increasing viscosity of the solvent (Figure 11), however, the change in k_d/k_c is not as pronounced as for the tert-butyl radical.

The shape of isopropyl radical is not spherical (Figure 12). This Figure shows two projections A and B of a space filling model of an isopropyl radical with its seven hydrogen atoms (white spheres), two methyl carbon atoms (black), and the central carbon (striped). The axis denoted by || is the symmetry axis

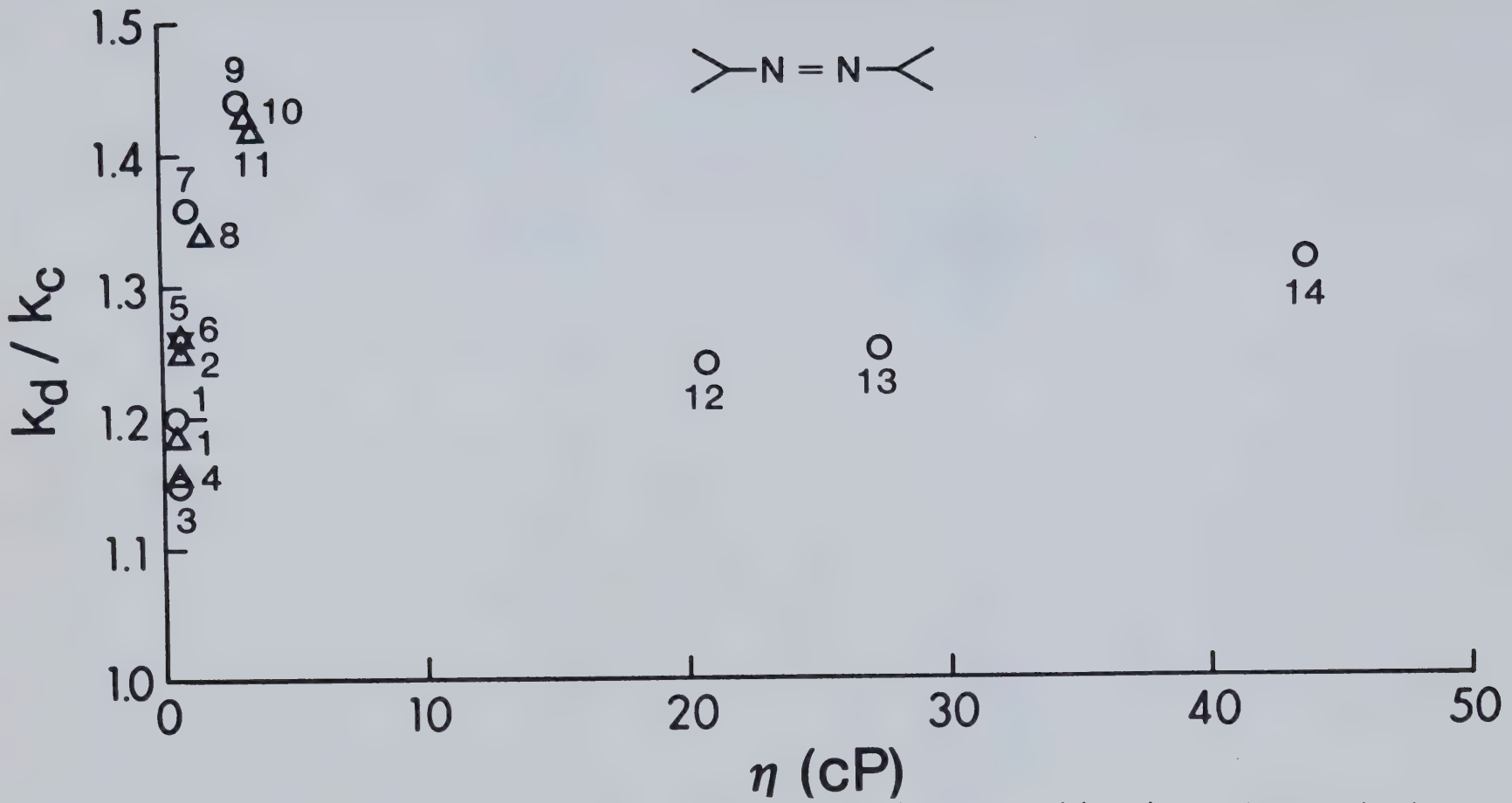


FIGURE 11. Plot of the ratio of cage disproportionation to combination rate constant, k_d/k_c, as a function of solvent viscosity, η. (The symbol △, correspond to the points in Table 19 and symbol ○, correspond to the points in Table 20 for the photodecomposition of azoisopropane).

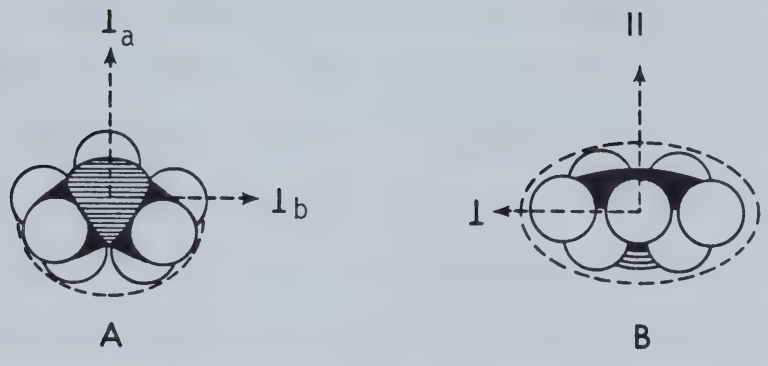


FIGURE 12. Two projections of a space-filling model of the isopropyl radicals.

of the half-occupied p-orbital.

Because of the shape of the isopropyl radical, the motion about the two perpendicular axes ($\perp_a, \perp_b$) are not equivalent. The perpendicular motion about $\perp_a$ axis is more hindered than the motion about $\perp_b$ axis (the perpendicular motion about $\perp_a$ axis for isopropyl radical is similar to the perpendicular motions about $\perp$ axes for tert-butyl radical). Since only motions about the $\perp$ axes lead to combination product, it would be expected that the rate of combination for isopropyl radicals increases relative to tert-butyl radicals. However, reorientation about the $\parallel$ axis appears to be hindered compared to the symmetrical tert-butyl radical and since this motion leads to disproportionation product, the relative ratios of k_d/k_c, as a function of viscosity of the media would be predicted, to be smaller than that observed for the tert-butyl radical. This crude approximation has been substantiated by the fact that k_d/k_c ratios for tert-butyl radical changed in benzene (η^{30} = 0.58 cP) from 5.0 to 7.2 in di-phenylether (η^{30} = 3.07 cP), approximately 45% change (Table 21). However, for isopropyl radical k_d/k_c ratios changed from 1.2 in benzene to 1.44 in di-phenylether, approximately ~20% change (Table 20).

The difference between cumyl radicals which couple to an extent of 94% and tert-butyl radicals, which disproportionate about 80% of the time, is still an

anomaly.[63] Nelsen and Bartlett[63] tried to rationalize this difference by invoking the delocalization of the odd electron in the cumyl radical. It was suggested that perhaps this delocalization diminishes the importance of hyperconjugation in the transition state for disproportionation. However, one might expect a lowering of the coupling rate for the same cause. For this reason the change in the k_d/k_c ratios on going from tert-butyl to cumyl radical could not be predicted. Further, comparison of the k_d/k_c ratio of our results for isopropyl radicals (~1.2 in benzene) to k_d/k_c ratio for cumyl radicals (~0.06 in benzene)[73] clearly shows that there is more than a statistical factor (number of β-H), which controls the disproportionation-combination ratio, since both isopropyl radical and cumyl radical have 6 β-Hs.

It is clear that more research is necessary to find out the factor or factors that might influence the absolute values of k_d/k_c ratios for different radicals.

Conclusion

The importance of polar effects in free radical reactions from substituted alkanes has been repeatedly demonstrated.[26] The suggestion that these effects may be interpreted as being governed solely by the

effect of the substituents on the bond strength of the bonds made and broken, ΔH, can not accommodate the experimental data,[26] i.e., the reversal of isomer distribution patterns found for the reactions of different polar radicals on a particular substrate.

The demonstrated nonlinearity of the correlation between ΔH and ρ (all negative ρ values) obtained for benzylic hydrogen abstraction rules out the bond dissociation energy as being the major contributing factor.[18] The demonstration that nucleophilc radicals can give a positive ρ value would further substantiate the importance of polar effects in governing the reactivity of these radicals.

The positive ρ value reported for the undecyl[40] radical has been questioned by Zavitsas.[43]

The positive ρ values reported for tert-butyl and isopropyl radicals[38,39] have been shown by Tanner et al.[46] and this work, to either show no correlation (BPP decomposition) or to be an artifact of an experimentally observed cage disproportionation reaction (AIB and AIP decompositions). The relatively selective tert-butyl and isopropyl radicals do not abstract hydrogen from solvent toluene (8-6 M) in competition with abstraction of deuterium from thiophenol-d at concentrations ranging from 0.6 to 3 M (for tert-butyl) and 0.5 M (for iso-

propyl). At lower concentrations of thiophenol-d (~0.1 M) the reaction begins to be measurably competitive (see Table 12 for isopropyl); however, the concentration of thiophenol-d cannot be approximated as constant and the kinetic expression could not be evaluated in the manner used.

It seems doubtful that any authentic positive ρ values have, as yet, been reported for benzylic hydrogen abstraction. Most likely this is due to the small difference between electronegativity of the carbon-centered radicals and the substrate benzylic carbon, while the absence of any correlation (zero or very small positive or negative values) attests to the small effect of small changes in BDEs. However positive rho values are observed[11] in halogen atom transfer reactions which have been used as models for hydrogen atom transfer. This class of substituent effects has been demonstrated in free radical chain reaction of the reduction of benzyl halides by tri-n-butylstannane.

The variation of disproportionation-combination ratios of alkyl radicals, as a result of carrying out the reactions, in different solvents were discussed. Possible factors which might influence this ratio were considered. It was originally thought[100] that disproportionation and combination have different activation

energies since the ratio of k_d/k_c was temperature dependent. It was subsequently shown[73] that this interpretation was not valid since it was found that the k_d/k_c ratio was a function of viscosity of the medium which was in turn being affected by temperature. The internal pressure argument, developed by Stefani[52,68] has been questioned.[64] Only recently Fischer's collision model[73] unambiguously defined the viscosity dependence of k_d/k_c for tert-butyl radicals obtained from encounter pairs. Fischer suggests that this model could be applied to other radicals.

Generation of geminate tert-butyl radical pairs by photolysis of 2,2'-azoisobutane (this work) and measurement of k_d/k_c demonstrated that at low viscosity, Fischer's model can be applied to geminate radical pairs. However at higher viscosities, deviation from Fischer's model was attributed to the geometry of the radical at birth.

Using Fischer's collision model, it was possible to rationalize the results of k_d/k_c ratios obtained for isopropyl radicals (geminate pair) in different solvents.

EXPERIMENTAL

Materials.

All solvents were purified before use. n-Heptane (MC & B Co.) and tetradecane (Aldrich Chemical Co.) were washed several times in succession with concentrated sulfuric acid, 10% aqueous sodium bicarbonate, and distilled water. The solvents were dried over anhydrous magnesium sulfate and fractionally distilled through a column packed with glass helices. GLC analysis (20 ft. x 1/8 in. 10% QF-1 on 80-100 Chromosorb WAW-DMCS, glass column) showed that they were >99.5% pure.

Toluene, p-xylene (Phillips 66 research grade >99.9%) and chlorobenzene (Aldrich Chemical Co.) were fractionally distilled through a column packed with glass helices and shown by GLC (QF-1 column) to be >99.9% pure.

m-Xylene (Phillips 66, >95%) was fractionally distilled using a 24-in. Teflon spinning band and shown by GLC to be >99% pure.

Benzonitrile (BDH) benzene (Fisher Scientific Co.), diphenyl ether, p-cyanotoluene, m-chlorotoluene and p-chlorotoluene (Aldrich Chemical Co.) were purified by repeated low temperature fractional recrystallization, fractionally distilled and checked for purity, 99.8%, by GLC (QF-1 column).

The paraffin oils (MC & B and BDH) were heated to 180° at 0.5 mm for 48 h in order to eliminate any

low boiling hydrocarbons. The paraffin oils were also checked for olefin impurities; since no color was observed on treatment with concentrated sulfuric acid, they were used without further purification.

Fluorolube oil was heated to 180° at 0.5 mm for 48 h and used without further purification.

tert-Butyl alcohol (Fisher Scientific Co.) and pinacol (Fluka) were fractionally distilled and checked for purity: >99.9%, by GLC (20 ft. x 1/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb WAW DMCS, glass column).

p-Phenoxytoluene was prepared using the Ullmann ether synthesis[101] and purified by fractional distillation (bp. 103-105°, at 2.5 mm) [lit.[102] bp. 277-278° (745.5 mm)]. NMR (CCl_4): δ 2.65 (s, 3H, $-CH_3$), 8.0-8.65 (m, 9H, aromatic). The GLC analysis (QF-1 column) showed this compound to be >99.7% pure.

Thiophenol (Aldrich Chemical Co.) was fractionally distilled and shown to be >99.5% pure by GLC (Carbowax Column).

Isobutane, isobutylene, propane, propylene, 2,3-dimethylbutane (Phillips research grade) and 2,2,3,3-tetramethylbutane (Aldrich Chemical Co.) were used without further purification.

Thiophenol-d was prepared as described by Pryor and Davis[39] by shaking thiophenol (previously distilled) with D_2O (Merck, Sharp and Dohme, Canada, >99.8% D) eight separate times. The thiophenol-d was dried

over anhydrous magnesium sulfate, decanted, and fractionally distilled under nitrogen (bp. 52°, 12 mm). The thiophenol-d was stored in sealed vials in 0.5 ml quantities over D_2O (1 drop in each vial). The NMR spectrum of the purified thiol showed it to be more than 97% deuterated.

AIB and AIP were prepared by the method of Stowell.[102] The azo compounds were fractionally distilled using a 24-in. Teflon spinning band column. AIB [bp. 106-107° (690 mm); NMR ($CDCl_3$) δ 1.15 (s, $C(CH_3)_3$); UV (C_6H_6) λ_{max} 370 nm (ε 26)] (lit. bp. 98-109,[103] 109-110);[104] GLC analysis (Carbowax column) showed this compound to be 99.5% pure. AIP [bp. 85° (690 mm); NMR ($CDCl_3$) δ 1.2 (d, J = 6.5 Hz, 6H), and δ 3.5 (septet, J = 6.5 Hz, 1H); UV (C_6H_6) λ_{max} 360 nm (ε 15)], [lit. bp. 40-41° (120 mm),[39] bp. 88.5°[105]]. GLC analysis using the Carbowax column showed this compound to be >98% pure. The main impurity was pentane, used as a solvent in the preparation of AIP.

Isopropyl hydrazone was prepared by the method of Ioffe:[71] bp. 125-126° (690 mm); NMR ($CDCl_3$) δ 1.12 (d, 6H, J = 6.5 Hz), 1.72 (s, 3H), 1.9 (s, 3H), 3.3 (septet, H, J = 6.5 Hz), 4.15 (broad, 1H) [lit.[106] bp. 132.8° (772 mm)].

Isobutyl and propyl phenyl sulfide were prepared according to the method of Ipatieff:[107] Isobutyl phenyl sulfide [bp. 100-102° (11 mm); NMR ($CDCl_3$) δ 1.01 (d, 6H), J = 5.96 Hz, CH_3), 1.86 (m, 1H, H-2), 2.79 (d, 2H,

J = 1.70 Hz, CH_2), 7.3 (m, 5H, aromatic)], and propyl phenyl sufide [bp. 79° (5 mm); NMR ($CDCl_3$) δ 1.02 (t, (3H, J = 7 Hz,), 1.7 (m, 2H, J = 7 Hz), 2.94 (t, 2H, J = 7 Hz), 7.32 (m, 5H, aromatic)].

Isobutylbenzene was prepared by the Clemmensen[108] reduction of isobutyrophenone [bp. 165° (690 mm), NMR ($CDCl_3$) δ 0.9 (d, 6H, J = 6 Hz), 1.83 (m, 1H, J = 6 Hz).

p-Cyano-tert-butylbenzene was prepared by dehydration of the corresponding amide using phosphorus pentoxide[109] [bp. 85-86° (6 mm), NMR ($CDCl_3$) δ 1.35 (s, 9H) and 7.58 (m, 4H, aromatic)], lit.[110] bp. 132-133° (21 mm).

The reactions were carried out in 20-mL Pyrex tubes equipped with break-seals. Prior to the photolysis all the tubes were washed successively with chromic acid, water, concentrated ammonium hydroxide, distilled water and dried. For the reactions to be carried out in the presence of thiophenol-d, the tubes were treated with several milliliters of D_2O, heated to reflux for several minutes and dried again overnight.

Photodecomposition of AIP in the Presence of PhSD.

Solutions of AIP and thiophenol-d were weighed into a volumetric flask and the materials were dissolved in the appropriate toluene to give the desired concentrations. An aliquot of the solution was transferred to the Pyrex reaction vessel, degassed by four freeze-thaw

cycles, and sealed. The portion of the the vessel above the liquid was covered with foil, and the vessel was placed in a Rayonet photochemical reactor (3500-Å BL lamps) and irradiated for 20 h (30°). The reaction vessel was connected to the vacuum line (A) shown in Figure 13, frozen (-198°) and opened. The noncondensable gases were passed through three traps D, E and F (-198°), and measured with the aid of a Toepler pump (G) using a calibrated volume and a transit to read the mercury levels. A sample of the gas collected was subjected to mass spectral analysis and was shown to contain H_2, HD and D_2. The relative amounts of the isotopic hydrogen and nitrogen were determined by vacuum line GLC (I) using a Cow Mac TR-TH thermal conductivity GLC fitted with a 10 ft. x 1/4 in. activated molecular sieve 13x glass column (H) at 0°, Argon was used as a carrier gas. The relative areas were determined using a HP-3380 A integrator. No attempt was made to separate the hydrogen isotopes.

The solution remaining in the reaction vessel was distilled through two -130° traps (D), and (E) (pentane/liquid nitrogen) into a trap at -198° (liquid nitrogen). The condensable gases, C_3H_8, C_3H_7D and C_3H_6, were collected and their total absolute amount was measured using the Toepler pump. The relative amounts were determined by vacuum line GLC (I) fitted with a 3 ft. x 1/4 in. activated alumina, glass column,

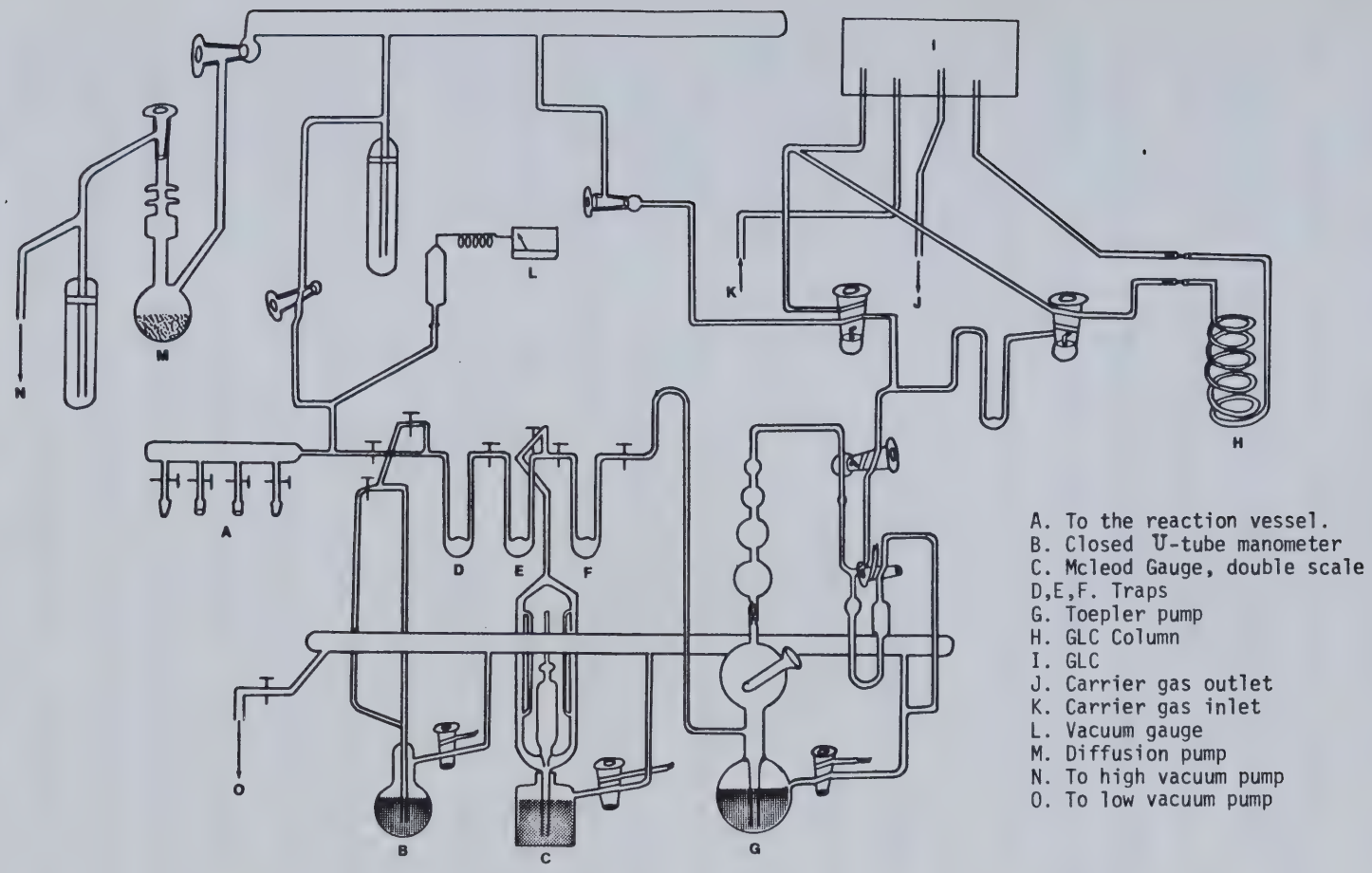


FIGURE 13. Vacuum line for isolation and analysis of gaseous products.

20°. The condensable gases were sealed in break-seals and submitted for mass spectral analysis. The residual reaction mixture was transferred back into the reaction vessel by warming traps (D) and (E) and cooling the original reaction vessel to -198°. After removing the reaction vessel from the vacuum line, a known amount of standard (nonane, decane, undecane, dodecane or hexadecane) was added to the mixture and the mixture was subjected to GLC analysis (QF-1 and Carbowax columns).

The products, 2,3-dimethylbutane and phenyl propyl-2-d sulfide, were identified by comparing their mass spectral cracking patterns and their GLC retention times with those of authentic samples (the retention time of the nondeuterated sulfide was used for that of the deuterated material). The mass spectrum of the synthesized sulfide showed a parent peak at m/e 152 ($C_9H_{12}S$) and no detectable fragmentation at m/e 151. The sulfide obtained from the reaction mixture showed a parent ion at m/e 153 ($C_9H_{11}DS$) and an ion at m/e 152 ($C_9H_{12}S$). The m/e 152/153 was about 20%. The remaining azoisopropane and isopropyl hydrazone, (the rearrangement product from the azo compound) were identified by a comparison of their GC/IR and GLC retention times with those of authentic samples. It was shown by direct injection of azoisopropane into the GLC system that no rearrangement took place and that

the azo compound did not decompose during GLC analysis. The results of a representative number of these analyses are listed in Table 10.

Photodecomposition of AIP in the Presence of PhSH.

Samples of AIP and thiophenol were weighed into a volumetric flask and the materials were dissolved in the appropriate solvent to give the desired concentration. An aliquot of the solution was transferred to the Pyrex reaction vessel, degassed by the freeze-thaw method, and sealed. The samples were irradiated as before for 20 h (30°). The reaction vessel was connected to the vacuum line at (A), (see Fig. 13) and the gaseous products were analyzed as before. A sample of the noncondensable gases collected was subjected to mass spectral analysis and was shown to contain hydrogen. The relative amounts of hydrogen and nitrogen were determined as previously described. The solution remaining in the reaction vessel was distilled through two -130° (D), and (E) traps into a trap (F) at -198°. The condensable gases C_3H_8 and C_3H_6 were collected and their total absolute amount was measured in the Toepler pump (G). Their relative amounts were then determined by vacuum line GLC (I) using the activated alumina column. For the reactions which were carried out in highly viscous solvents such as Nujol, it was necessary to warm up the

reaction vessel to ~50° to make sure that all the propane and propene have been distilled. Propane and propene were identified by a comparison of their mass spectral cracking pattern and their GLC retention times with those of authentic samples.

The residual reaction mixture was transferred back into the reaction vessel by warming the traps (D) and (E) to room temperature and cooling the reaction vessel to -198°. After removing the reaction vessel from the vacuum line, a known amount of standard (nonane, decane, undecane, or hexadecane) was added and the mixture was subjected to GLC analysis (QF-1 or Carbowax column).

The remaining products, 2,3-dimethylbutane, isopropyl hydrazone and the unreacted azoisopropane were identified as before. Phenyl propyl sulfide was identified by its mass spectral cracking pattern and its GLC retention time compared with that of an authentic sample. The results of a representative number of these analysis are listed in Table 11.

Photodecomposition of AIP in Benzene.

The reaction of AIP in benzene was carried out and gaseous products were analyzed in the manner described above. The remaining material was condensed back into the reaction vessel and removed from the vacuum line.

A known amount of standard (dodecane or hexadecane) was added to the mixture and the mixture was subjected to GLC analysis, (Carbowax column).

The remaining products, 2,3-dimethylbutane, a small amount of isopropylhydrazone and unreacted AIP were identified as previously described. The GLC analysis showed the presence of another peak which accounted for ~6% of the isopropyl radicals produced. This product was identified as isopropyl benzene by comparing its IR spectrum, mass spectral cracking pattern and GLC retention time with an authentic sample. The GLC analysis also showed the presence of >7 products (~12%) which were not identified. The results of a representative number of these analyses are listed in Table 13.

Photodecomposition of AIP in Toluene.

The reaction of AIP in toluene was carried out and analyzed in the same manner as described for the AIP decomposition in benzene. The GLC analysis (Carbowax column) of the solution showed the presence of 2,3-dimethylbutane, small amount of isopropyl hydrazone and unreacted AIP. These products were identified as before. One of the (>11) minor products (~6%) formed was identified as isobutylbenzene by comparing its IR spectra and GLC retention time with that of authentic sample. Subsequently, it was shown, by the use of GLC capillary

column chromatography, (50 m x 0.02 mm methyl silicon fluid, SP-2100, Carbowax 20 m deactivated, 50°) that this compound contained two other products (~1%). The products were tentatively identified (GLC retention time) as p-isopropyl toluene and o-isopropyl toluene. Along with these products, bibenzyl (4.4%) was formed. This compound was identified by its mass spectral cracking pattern, IR spectrum (GC/IR) and GLC retention time compared with an authentic sample. The results of a representative number of these analyses are listed in Table 13.

No attempt was made to quantitatively determine the amounts of phenyl disulfide and diphenyl sulfide obtained in the reactions carried out in the presence of thiophenol. The products, 2-methylpentane, 4-methyl-1-pentene and 4-methyl-2-pentene, that were likely to be formed in the reaction of isopropyl radicals and propene, were specifically searched for (GLC) and were found to be undetectable.

Photodecomposition of AIB in the Presence of PhSH.

Solutions of AIB and thiophenol were weighed into a volumetric flask and the materials were dissolved in the appropriate solvent to give the desired concentration. An aliquot of the solution was transferred to a Pyrex reaction vessel, degassed by the freeze-thaw method

(three times), and sealed. The portion of the vessel above the liquid was covered with foil, and the vessel was placed into a Rayonet photochemical reactor (3500 Å BL lamps) and irradiated for 14 hr (30°). The reaction vessel was connected to the vacuum line at (A) (see Fig. 13), frozen (-198°) and opened. The noncondensable gases were measured as previously described. A sample of the gas collected was subjected to mass spectral analysis and was shown to contain a negligible amount of hydrogen.

The solution remaining in the reaction vessel was distilled through two -78° traps (D), and (E) (using dry ice acetone) into a trap at -198° (liquid nitrogen). However, for the reactions which were carried out in solvent n-heptane, it was necessary to use two traps at -110° (isobutyl alcohol/liquid nitrogen) instead of -78°, in order to prevent the co-distillation of the solvent. The condensable gases, isobutane and isobutylene were collected and their total absolute amount was measured using the Toepler pump. The relative amounts were determined by vacuum line GLC (I) fitted with a 10 ft. x 1/4 in. 10% silicon oil 200 on 60/80 chromosorb WAW glass column, 0°. For the reactions which were carried out in highly viscous solvents such as Nujol, it was necesary to warm up the reaction vessel to ~50° to make sure that all the isobutane and isobutylene have been distilled. Isobutane and iso-

butylene were identified by their mass spectral cracking pattern and their GLC retention times compared with those of authentic samples. The residual reaction mixture was transferred back into the vessel by warming traps (E) and (D) to room temperature and cooling the original reaction vessel to (-198°). After removing the reaction vessel from the vacuum line a known amount of standard (undecane, dodecane or hexadecane) was added to the mixture and the mixture was subjected to GLC analysis (Carbowax and QF-1 columns).

The remaining products, 2,2,3,3-tetramethylbutane and phenyl isobutyl sulfide, were identified by comparing their mass spectral cracking pattern and their GLC retention times with those of authentic samples.

No attempt was made to quantitatively determine the amounts of phenyl disulfide and diphenyl sufide obtained in the reaction. No other product could be detected. The products, 2,2,3-trimethylpentane, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, that were likely to be formed in the reaction of tert-butyl radicals and isobutylene, were specifically searched for (GLC) and were found to be undetectable. The results of these analyses are listed in Table 16.

Photodecomposition of AIB in Benzene.

A sample of AIB in benzene was prepared and the

photodecomposition and gas analysis was carried out in the same manner as described above. A sample of noncondensable gases collected was subjected to mass spectral analysis and was shown to be solely nitrogen. The residual reaction mixture was transferred into the reaction vessel and removed from the vacuum line. A known amount of standard (dodecane) was added to the mixture and the mixture was subjected to GLC analysis (Carbowax column). Beside the combination product, 2,2,3,3-tetramethylbutane, one of the (>4) minor products (~1.5%) was identified to be tert-butylbenzene by its mass spectral cracking pattern and its GLC retention time. The results of a representative number of these analyses are listed in Table 17.

Photodecomposition of AIB in Benzonitrile.

The reaction of AIB in benzonitrile was carried out and analyzed in the same manner as described for the AIB decomposition in benzene. The analysis of the remaining solution by GLC (Carbowax column) showed the presence of combination product, 2,2,3,3-tetramehtylbutane. One of the (>4) minor products (~7.5%) was identified as p-cyano-tert-butylbenzene by a comparison of its mass spectral cracking pattern and its GLC retention time with that of an authentic sample. Subsequently it was shown by using the methyl silicon

capillary column that the peak identified as p-cyano-tert-butylbenzene was a mixture of two compounds is an approximate 17:1 ratio. The GLC retention time of the larger peak was identical as p-cyano-tert-butylbenzene and the smaller peak was tentatively assigned the structure, o-cyano-tert-butylbenzene (Table 17).

GLC Analyses.

All analyses were carried out using a HP 5840-A gas chromatograph fitted with a flame ionization detector. All quantitative values reported were electronically integrated (HP 5840-A) and were determined using standard calibration curves obtained from known mixtures of authentic materials. The relative GC areas for gaseous samples were determined using the method of peak height x peak width at one-half peak height.

Viscosity Measurements.

The viscosities of the substituted toluenes, benzenes and all other solvents were determined at 30° using an Ostwald viscometer, calibrated using distilled water as a standard.[111]

Mass Spectrometry.

The high-resolution mass spectrometry was carried out using an AEI-MS50 mass spectrometer apparatus at a

resolving power of 25000. The GC-mass spectrometry was carried out using an AEI-MS 12 coupled to a Varian Aerograph 1400 GC fitted with the Carbowax or OF-1 columns. The MS 50 and MS 12 were coupled to an AEI DS50S data system.

GLC-IR Analyses.

The GC/IR analyses were carried out on kinetic reaction mixtures from the reaction of 0.1 M AIP and 0.5 M PhSD in p-cyanotoluene and on reaction mixtures from the reaction of 0.1 M AIP in benzene and toluene. The spectrum for each compound was obtained using a Nicolet 7199 FT-IR interfaced to a Varian series 3700 gas chromatograph fitted with the Carbowax or OF-1 columns. The spectrum of each compound was compared with that of the authentic material.

REFERENCES

1. F.M. Lewis, F.R. Mayo, and W.F. Hulse, J. Am. Chem. Soc., 67, 1701 (1945)
2. C.C. Price, J. Polym. Sci., 1, 83 (1946).
3. K. Nozaki and P.D. Bartlett, J. Am. Chem. Soc., 68, 1686 (1946).
4. C. Walling and B. Miller, J. Am. Chem. Soc., 79, 4181 (1957).
5. C. Walling, E.R. Briggs, K.B. Wolfstirn, and F.R. Mayo, J. Am. Chem. Soc., 70, 1537 (1948).
6. a) C. Walling, "Free Radicals in Solution", Wiley, New York, 1957.
   b) See review in J.K. Kochi, Ed., "Free Radicals", Vol. 1 and 2, Wiley, New York, 1973.
7. R.S. Davidson, Quart. Rev., 21, 249 (1967).
8. A.F. Trotman-Dickenson, Advan. Free Radical Chem., 1, 1 (1965).
9. J.M. Tedder, Quart. Rev., 14, 336 (1960).
10. G.A. Russell, J. Org. Chem., 23, 1407 (1958).
11. E.V. Blackburn and D.D. Tanner, J. Am. Chem. Soc., 102, 692 (1980).
12. F.R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).
13. W.A. Pryor and J.P. Stanley, J. Am. Chem. Soc., 93, 1412 (1971).

14. R.F. Bridger and G.A. Russell, J. Am. Chem. Soc., 85, 3754 (1964).

15. W.A. Pryor, K. Smith, J.T. Echols, Jr., and J.L. Fuller, J. Org. Chem., 36, 1753 (1972).

16. W.A. Pryor, U. Tonellato, D.L. Fuller, and S. Jumorville, J. Org. Chem., 34, 2018 (1969).

17. G.A. Russell and R.C. Williamson, J. Am. Chem. Soc., 86, 2357 (1964).

18. D.D. Tanner, R.J. Arhart, E.V. Blackburn, N.C. Das, and N. Wada, J. Am. Chem. Soc., 96, 829 (1974).

19. R.E. Pearson and J.C. Martin, J. Am. Chem. Soc., 85, 354, 3142 (1963).

20. a) C. Walling, A.L. Rieger. and D.D. Tanner, J. Am. Chem. Soc., 85, 3129 (1963).

    b) C. Walling and A.L. Rieger, ibid., 85, 3135 (1963).

21. See reference 6a, pp. 132-140, 365-369, 375-376, 417, 474-491.

22. W.A. Pryor, "Free Radicals", McGraw Hill, New York, N.Y., 166, p. 170.

23. D.C. Nonhebel and J.C. Walton, Free-Radical Chemistry", Cambridge University Press, London, 1974, pp. 178-185.

24. K.U. Ingold and B.P. Roberts, "Free Radical Substitution Reactions", Wiley-Interscience, New York, N.Y., 1971, p. 158.

25. E.S. Huyser, "Free Radical Chain Reactions", Wiley-Interscience, New York, N.Y., 1970, pp. 70, 143, 346, 358.

26. G.A. Russell in "Free Radicals", Vol. 1, J.K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp. 293-298.

27. W.A. Pryor, T.H. Lin, J.P. Stanley, and R.W. Henderson, J. Am. Chem. Soc., 95, 6993 (1973).

28. I.B. Afanasev, Russ. Chem. Rev. (Engl. Transl.), 40, 216 (1971).

29. M.J. Perkins in "Free Radicals", Vol. II, J.K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp. 244-253.

30. S.F. Nelsen and D.H. Heath, J. Am. Chem. Soc., 91, 6452 (1969).

31. P.N. Cote and B.M. Vittimberga, Tetrahedron Lett., 2397 (1972).

32. C. Walling and R.T. Clark, J. Am. Chem. Soc., 96, 4530 (1974).

33. See reference 26, p. 285.

34. A.A. Zavitsas and J.A. Pinto, J. Am. Chem. Soc., 94, 7390 (1972).

35. A.A. Zavitsas, J. Am. Chem. Soc., 94, 2779 (1972).

36. J.A. Howard and J.H.B. Chenier, J. Am. Chem. Soc., 95, 3055 (1973).

37. L.R. Mahoney and M.A. DaRooge, J. Am. Chem. Soc., 92, 4063 (1970).

38. W.A. Pryor, W.H. Davis, Jr., and J.P. Stanley, J. Am. Chem. Soc., 95, 4754 (1973).

39. W.H. Davis, Jr. and W.A. Pryor, J. Am. Chem. Soc., 99, 6365 (1977).

40. W.A. Pryor and W.H. Davis, Jr., J. Am. Chem. Soc., 96, 7557 (1974).

41. R.W. Henderson and R.D. Ward, Jr., J. Am. Chem. Soc., 96, 7556 (1974).

42. R.W. Henderson, J. Am. Chem. Soc., 97, 213 (1975).

43. A.A. Zavitsas and G.M. Hanna, J. Org. Chem., 40, 3782 (1975).

44. A.A. Zavitsas, G.M. Hanna, A. Arafat, J. Ogunwole, and L.R. Zavitsas, "2nd International Symposium on Organic Free Radicals", 17-23, July 1977, Paris, France.

45. D.D. Tanner, R. Henriquez, and D.W. Reed, Can. J. Chem., 57, 2578 (1979).

46. D.D. Tanner, P.W. Samal, T.G.S. Ruo, and R. Henriquez, J. Am. Chem. Soc., 101, 1168 (1979).

47. D.D. Tanner, H. Yabuuchi, and H. Lutzer, Can. J. Chem., 55, 612 (1977).

48. Unpublished work from this laboratory.

49. P.D. Bartlett and J.M. McBride, Pure Appl. Chem., 15, 89 (1967).

50. J.P. Lorand, J. Am. Chem. Soc., 96, 2867 (1974).

51. T. Koenig and H. Fischer in "Free Radicals", Vol. 1, J.K. Kochi, Ed., Wiley, New York, 1973, pp. 168-171.

52. P.S. Dixon, A.P. Stefani, and M. Szwarc, J. Am. Chem. Soc., 85, 2551, 3344 (1963).

53. J.N. Bradley and B.S. Rabinovitch, J. Chem. Phys., 36, 3498 (1962).

54. S. Kodama, S. Fujita, J. Takeishi, and O. Toyama, Bull. Chem. Soc. Japan, 39, 1009 (1966).

55. H.A. Gillis, Can. J. Chem., 49, 2861 (1971).

56. S.W. Benson and W. DeMore, Annu. Rev. Phys. Chem., 16, 397 (1965).

57. J.N. Bradley, J. Chem. Phys., 35, 748 (1961).

58. R.S. Konar, Int. J. Chem. Kinet., 3, 379 (1971).

59. K.J. Laidler, Int. J. Chem. Kinet., 3, 377 (1971).

60. H.D. Beckhaus and C. Rüchardt, Chem. Ber. 110, 878 (1977).

61. K. Hancock, E.A. Meyers, and B.J. Yager, J. Am. Chem. Soc., 83, 4211 (1961).

62. E_S^C for Cumyl radical was calculated according to the empirical method suggested by T. Fujita, C. Takayama, and M. Nakajima, J. Org. Chem., 38, 1623 (1973).

63. S.F. Nelsen and P.D. Bartlett, J. Am. Chem. Soc., 88, 137 (1966).

64. P.A. Sheldon and J.K. Kochi, J. Am. Chem. Soc., 92, 4395 (1970).

65. O. Dobis, J.M. Pearson, and M. Szwarc, J. Am. Chem. Soc., 90, 278 (1968).

66. K. Chakravorty, J.M. Pearson, and M. Szwarc, J. Am. Chem. Soc., 90, 283 (1968).

67. F.D. Greene, M.A. Berwick, and J.C. Stowell, J. Am. Chem. Soc., 92, 867 (1970).

68. A.P. Stefani, J. Am. Chem. Soc., 90, 1694 (1968).

69. J.M. McBride, J. Am. Chem. Soc., 93, 6302 (1971).

70. A.B. Jaffe, K.J. Skinner, and J.M. McBride, J. Am. Chem. Soc., 94, 8510 (1972).

71. R.D. Kelley, R. Klein, and M.D. Scheer, J. Phys. Chem., 74, 4301 (1970).

72. R. Klein, M.C. Scheer, and J.G. Waller, J. Phys. Chem., 64, 1247 (1960).

73. H.H. Schuh and H. Fischer, Helv. Chim. Acta, 61, 2463 (1978).

74. H.H. Schuh and H. Fischer, Helv. Chim. Acta, 61, 2130 (1978).

75. G. Allen, G. Gee, and G.J. Wilson, Polymer I, 456 (1960).

76. J. Frank and E. Rabinowitch, Trans. Faraday Soc., 30, 120 (1934).

77. R.M. Noyes, J. Phys. Chem., 18, 999 (1950); 22, 1349 (1954).

78. R.M. Noyes, J. Phys. Chem., 65, 763 (1961).

79. R.M. Noyes, Prog. Reaction, Kinetics, 1, 131 (1961).

80. T. Koenig, "Free Radicals", Vol. 1, J.K. Kochi, ed.; Wiley, N.Y., 1973 Ch. 4.

81. N. Nodelman and J.C. Martin, J. Am. Chem. Soc., 98, 6597 (1976).

82. Formation of hydrogen atoms by the photolysis of thiols is a well known process, see for example:
a) C. Walling and R. Rabinowitz, J. Am. Chem. Soc., 81, 1137 (1959).
b) W.A. Pryor and J.P. Stanley, J. Am. Chem. Soc., 93, 1412 (1971).

83. O. Exner, "Correlation Analysis in Chemistry", Chapman, N.B., Shorter, J., Eds.; Plenum: London, 1978.

84. E.S. Lewis and K. Ogino, J. Am. Chem. Soc., 98, 2260 (1976).

85. K.R. Kopecky and T. Gillan, Can. J. Chem., 47, 2371 (1969).

86. A.F. Bickel and E.C. Kooymann, Nature, 170, 211 (1952).

87. R.G. Peterson and S.D. Ross, Tetrahedron Lett., No. 23, 18 (1960).

88. See reference 6a, p. 157.

89. See reference 6a, pp. 95 and 157.

90. K.U. Ingold in "Free Radicals", Vol. 1, J.K. Kochi, Ed., Wiley, New York, 1973, p. 43.

91. B. Blank, A. Henne, and H. Fischer, Helve. Chim. Acta, 57, 920 (1974).

92. H.P. Waits and G.S. Hammond, J. Am. Chem. Soc., 86, 1911 (1964).

93. P.S. Engel and P.D. Bartlett, J. Am. Chem. Soc., 92, 5883 (1970).

94. a) T. Mill and R.S. Stringham, Tetrahedron Lett., 1853 (1969).

b) P.S. Engel and D.J. Bishop, J. Am. Chem. Soc., 97, 6754 (1975).

c) P.S. Engel, R.A. Melaugh, M.A. Page, S. Szilagyi, and J.W. Timberlake, J. Am. Chem. Soc., 98, 1971 (1978) (1978).

95. a) G. Zimmerman, L.Y. Chow, and U.J. Paik, J. Am. Chem. Soc., 80, 3528 (1958).

b) N.A. Porter and M.O. Funk, J. Chem. Soc., Chem. Commun., 263 (1973).

96. I.I. Abram, G.S. Milne, B.S. Solomon, and C. Steel, J. Am. Chem. Soc., 91, 1220 (1969).

97. a) H. Kiefer and T. Traylor, J. Am. Chem. Soc., 89, 6667 (1967).

b) T. Loenige, J. Am. Chem. Soc., 91, 2558 (1969).

c) M. Szwarc, papers presented at the 160th National Meeting of the American Chemical Society, Chicago, Illinois, Sept. 1970.

98. B. Booth and R.M. Noyes, J. Am. Chem. Soc., 82, 1868 (1960).

99. T. Koenig, J. Am. Chem. Soc., 91, 2558 (1969).

100. D. Griller and K.U. Ingold, J. Am. Chem. Soc., 97, 1813 (1975).

101. A.L. Williams, R.E. Kinney, and R.F. Brodger, J. Org. Chem., 32, 2504 (1967).

102. F. Ullmann and P. Sponajel, Ann. 350, 83 (1906).

103. J.C. Stowell, J. Org. Chem., 32, 2360 (1967).

104. E. Farenhorst and E.C. Kooyman, Recl. Trav. Chim. Pays-Bas, 72, 993 (1953).

105. R. Renaud and L.C. Leitch, Can. J. Chem., 32, 545 (1954).

106. B.V. Ioffe, V.S. Stopskii, and Z.I. Sergeeva, J. Org. Chem. USSR, 4, 957 (1968).

107. V.N. Ipatieff, H. Pines, and B.S. Friedman, J. Am. Chem. Soc., 60, 2731 (1938).

108. A.I. Vogel, "Practical Organic Chemistry", Longman, London, p. 238.

109. See reference 108, p. 803.

110. L. Harvey, G.J. Gleicher, and W.D. Totherow, Tetrahedron, 25, 5019 (1969).

111. F. Danels, J.W. Williams, P. Bender, R.A. Alberty, C.D. Cornwell, and J.E. Harriman, "Experimental Physical Chemistry", 7th ed., McGraw-Hill, New York, 1978, p. 164.

APPENDIX

Error Analyses

Since all the product analyses in this work were carried out using GLC, one should take into account, the error which is involved in the analytical procedure. The error analysis was carried out for a large number of the experiments and it was shown that the percentage of the error was within the reproducibility of the experiment. In the following a few examples of error analysis are given.

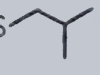
Limit error for additions and divisions were calculated as:

$$\text{Addition:} \quad \Delta Z = |\Delta X| + |\Delta Y|$$

$$\text{Division:} \quad \frac{\Delta Z}{Z} = \left|\frac{\Delta X}{X}\right| + \left|\frac{\Delta Y}{Y}\right|$$

1) Error analysis for % cage and k_d/k_c (point 1-2 page 128)

GLC Analysis

Compound	Quantities mmol 1	Quantities mmol 2	Average	Δ
	0.018735	0.018867	0.018801	0.000132
PhS 	0.086328	0.085840	0.086084	0.000488

a) % cage:

% cage = + PhS = 0.104885

Error = 0.00062

% error = 0.00062 ÷ 0.104885 = 0.6%

b) k_d/k_c:

k_c/k_c obtained = 4.57 ± 0.5

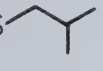
$$\frac{\Delta Z}{4.57} = \frac{0.000488}{0.086084} + \frac{0.000132}{0.018801}$$

$$\frac{\Delta Z}{4.57} = 0.0056688 + 0.0070209$$

$$\Delta Z = 0.058$$

2) Error analysis for % cage and k_c/k_c (point 13-14 page 128)

GLC Analysis

Compound	Quantities mmol 1	Quantities mmol 2	Average	Δ
	0.023706	0.0239389	0.023572	0.00073
	0.020426	0.02076	0.020593	0.00034
PhS 	0.117998	0.11640	0.117199	0.001593

a) % cage = + + PhS = 0.161364

Error = 0.002669

% error = 0.161364 ÷ 0.002668 = 1.65%

b) k_d/k_c:

k_d/k_c obtained = 6.74 ± 0.16

$$\frac{\Delta Z}{6.74} = \frac{0.00073}{0.023572} + \frac{0.00034}{0.020593} + \frac{0.001593}{0.117199} + \frac{0.00034}{0.020593}$$

$$\Delta Z = 0.5$$

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